

OPTICAL PROPERTIES OF SATELLITE SURFACE MATERIALS

THE THEORY OF OPTICAL AND INFRARED

PROPERTIES OF METALS

by

E. E. H. SHIN

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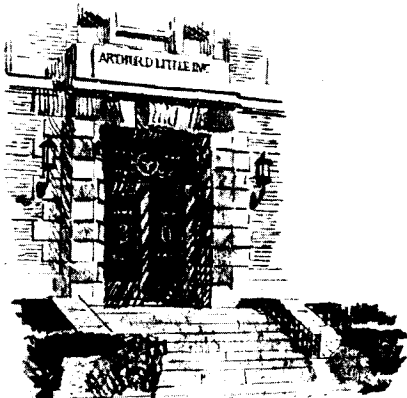
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E. E. H. SHIN

Final Report, Part III

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ABSTRACT

Existing theoretical descriptions of the optical properties of metals fail to explain measured characteristics particularly at short wave lengths and at low temperatures. This failure may be attributed to incorrect interpretation of the physical mechanism responsible for optical and infrared dispersion. A comprehensive theory based on a perturbation treatment of bulk electron-phonon processes is presented here. The central feature of the theory is the derivation of the quantum correction factor which, when multiplied by the d.c. damping coefficient, gives the frequency-dependent damping coefficient. The theory is then combined with the already existing theories of Umklapp and impurity scattering processes. The theory successfully accounts for the optical properties of metals in the entire free electron region at all temperatures of practical interest.

Detailed calculations are presented for monovalent metals and some polyvalent metals for which assumption of a symmetric Fermi surface is valid. Polyvalent and transition metals for which interband transitions are important and the Fermi surface is not spherical are also considered. In all more than a dozen metals for which reliable experimental data are available have been successfully treated.

Calculations of the absorption properties of superconducting metals are also presented in an attempt to determine the extent to which bulk electron-phonon processes are responsible for infrared absorption by super-conductors.

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Chapter I

Introduction

The interactions of metals with an external electromagnetic field manifest themselves in different forms depending on the different spectral ranges that are involved. Two particular examples may be cited, the d.c. electrical properties which we observe by applying a static electric field, i.e. the zero-frequency limit and the optical and infrared dispersion characteristics which are observed by means of proper optical apparatus where the frequency spectrum extends from the far infrared to the ultraviolet.

The present work is concerned with the normal dispersion characteristics in the optical and infrared range of the spectrum and the manner in which these properties are related to the d.c. electrical properties and other lattice parameters of metals. Inasmuch as we are concerned with normal dispersion in contrast to anomalous dispersion, the frequency spectrum that is involved in the present work must be sufficiently removed from the anomalous region in which photoelectric resonances of bound electrons become important. Most of the metals that have been studied are found to have their lowest resonances in the wavelength region, $0.3 \sim 1.0$ micron, and normal dispersion is observed for wavelengths longer than these values.

According to the free electron theory of metals, the free, valence-electrons are responsible for the normal dispersion of optical and infrared waves as well as for electrical conduction.

Ever since the discovery of electrons and Sommerfeld's successful explanation of the phenomenon of thermionic emission based on the free electron picture of metals and on the Thomas-Dirac statistics, it has been a popular notion that both optical dispersion properties and electrical properties may be explained on a common theoretical basis and that these two aspects of metallic properties are inter-related in a rather simple manner. Granted that the simple free electron description of metals is valid, such a notion finds justification in that both the optical dispersion and d.c. electrical properties are described by the equation of motion of the conduction electrons subject to the general description in terms of Maxwell's equations, the difference between the two aspects of metallic properties arising solely from the different spectral ranges that are involved.

Therefore, it may be expected that various frequency-dependent optical quantities such as the optical conductivity $\sigma(\omega)$ and the dielectric constant $\epsilon(\omega)$ which describe the optical dispersion properties, should also describe the d.c. electrical properties such as the d.c. electrical conductivity σ_0 and dielectric constant ϵ_0 when we take the limit $\omega \rightarrow 0$ in various dispersion equations. On the other hand, the temperature-dependence of various optical quantities may be predicted from the more widely studied electrical properties.

Along with the development of quantum mechanics and quantum statistics, much progress has been made on the theory of electrical conduction in metals during the past fifty years, and current theory is successful in explaining the observed electrical conduction phenomena both qualitatively and quantitatively in most of the noble and alkali metals, and qualitatively in the transition metals. Modern physics is successful in explaining qualitatively some of the salient features found in alloys, e.g. Matthiessen's rule, dependence of resistivity on the relative concentrations of the constituent metal atoms in a random alloy, some unusual properties of the transition metal alloys, etc. Compared with what has been done on the electrical properties of metals, surprisingly little progress has been made on the theory of optical and infrared dispersion in metals. In fact, there is no satisfactory theory available that can predict the dispersion properties in the entire free electron part of the spectrum of even the noble and alkaline metals. Existing theories enjoy a limited success in various segments of the spectrum. However, the less said the better with regard to the transition metals and alloys. This is surprising for theoretically, a description of optical and infrared dispersion properties is expected to be very much like that of electrical properties, at least to the extent that both involve free conduction electrons, and differ from each other only in the

extra frequency-dependence appearing in the optical quantities.

Theoretical discussions on the behavior of metallic conductors under the influence of electromagnetic waves were first given by Hagen and Rubens on the basis of the classical Maxwell theory of electrodynamics, and later by Drude on the basis of the free electron description of metals and Maxwell's theory. Drude's theory applies to a wider range of the spectrum than the Hagen-Rubens theory, and the two theories are identical at the longer wavelengths where the optical conductivity $\sigma(\omega)$ can be replaced by the d.c. conductivity $\sigma(0)$.

The limitations that are inherent in these theories have been pointed out in a number of references upon comparison with experimental data. In general, the theories fail in the higher frequency region of the spectrum (i.e., $\hbar\omega \gtrsim kT$) and also at low temperatures. The Drude theory has found a qualitative success in a variety of metals in that it offers a good fit to the experimental dispersion curves, and yet fails quantitatively in that the d.c. conductivity predicted by the best-fit theoretical curves is always smaller than the measured values. The exceptions are some liquid metals such as mercury and gallium. In any case, the theory fails completely at low temperatures. Despite these limitations, the classical free electron

theory of Drude has remained the most successful of the existing theories in the sense that it presents all aspects of dispersion properties in a rather self-contained manner, especially when combined with the Kramers-Kronig relation. Although there have been some attempts made to improve the Drude theory so that it would be applicable to a wider range of the spectrum and to extend it to multivalent and transition metals, they fail to remove the limitations that are inherent in the original Drude theory since these attempts were not made through a rigorous theoretical formulation but rather by introducing additional unknown parameters.

According to the classical theory, the optical absorptivity (= emissivity) of a pure metal vanishes at very low temperatures in contrast to experimental observations, and a metal can have a nonvanishing absorption or resistivity (Restwiderstand) only if a substantial amount of impurities is present. Although the theory of anomalous skin effect (i.e., anomalous in the sense that the distance traveled by an electron between collisions is larger than the skin depth, $l = v_F \tau > \delta_s$) proposed by Reuter and Sondheimer and later elaborated by Dingle has succeeded in explaining a part of the observed absorption at low temperatures, the gap between the theoretical and experimental values still remains to be accounted for and amounts to anywhere between 20% ~ 80% of the measured values of the total absorptivity.

Practically all of the existing quantum mechanical theories of optical and infrared absorption in metals have been developed since 1954, and were designed to remedy the gap between the classical theoretical values and the observed values of the absorptivity in the near infrared and at low temperatures. However, none of these theories show attempts to formulate different aspects of the optical and infrared dispersion properties in such a self-contained form as is possible in the classical Drude theory. They are confined to derivations of absorptivity as a function of temperature and wavelength in a particular segment of the infrared spectrum. The most outstanding of these theories are those of Holstein, and those developed more recently by Gurzhi and Silin of Russia. It was Holstein who originally suggested that, unlike what is predicted by the theory of anomalous skin effects, a bulk absorption process in which an electron absorbs a photon near the surface and then diffuses into the bulk interior of the lattice emitting a phonon to conserve energy and momentum, may play a significant role at low temperatures. Holstein calculated absorptivity in the near infrared region ($\lambda \sim 1\mu$), and the results were already sufficient to prove that, at low temperatures too, the bulk electron-phonon collisions are not less important than the skin effects of Reuter, Sondheimer and Dingle. More recently, Gurzhi made an attempt to formulate the total absorptivity

including both the skin effects and the Holstein's bulk mechanism to be applicable to a wider range of spectrum than what is defined by $\hbar\omega \gg K\Theta \gg KT$. Gurzhi's result was, at least, in its form more general than that of Holstein's formulae, and will be shown to agree identically with the absorptivity derived in the present work in the limit, $\hbar\omega \gg K\Theta, KT$. Following the semi-classical calculations by Silin of the contribution by the electron-electron collisions to the absorptivity based on the Fermi-liquid theory of Landau, Gurzhi improved Silin's method by use of a more rigorous Fermi-liquid theory. He pointed out that the electron-electron collisions may be significant at high frequency and at low temperature, and subsequently incorporated these into his previously obtained formula for the total optical absorptivity. The theoretical method used by Gurzhi is essentially that of obtaining perturbation solutions to the kinetic equation for the electron distribution functions taking into account various collision terms. This is very much like what was done by Wilson in his calculations of various d.c. electrical properties. Holstein used a straightforward quantum mechanical perturbation theory and calculated various transition matrix elements using a semi-classical form of electromagnetic perturbation. There are, of course, other sophisticated theoretical techniques available for calculating the optical properties of metals such as the method of temperature-dependent Green's functions developed

by Martin and Schwinger and independently by Kogan, and also the S-matrix formulation which was used by Gurevich and Uritskii in their theory of infrared absorption in crystals, mainly for semi-conductors, in the presence of external magnetic field and in the photoelectric region. However, the remarkable success found in the results obtained by Holstein and Gurzhi in the high frequency region, and also in the results obtained in the present work for a wider range of spectrum attest to the fact that a straightforward quantum mechanical perturbation theory is satisfactory for both qualitative and quantitative calculations of the optical properties, at least in the free-electron region of the spectrum. On the other hand, a quantitative calculation of optical properties in the resonance region (i.e., for $\lambda \lesssim 1\mu$ for many metals) can be offered when the general results obtained on photoelectric absorption in crystals such as that by Gurevich and Uritskii, are extended to include the resonance absorption in metals.

The main body of the present work consists of calculations of various optical and infrared dispersion and electrical properties as well as other related lattice parameters based on Holstein's bulk mechanism. In this sense, the theory by Gurzhi is the closest to the present work inasmuch as it is also based on the same mechanism for electron-phonon processes. Although Gurzhi's formula for absorptivity

agrees with the present theory identically in the near infrared where $\hbar\omega \gg kT$, there are some important differences between the two, and the shortcomings of Gurzhi's theory will be explained.

A theory may be judged on the basis of the following obvious set of criteria:

- a) It has to provide a good fit in frequency-dependence to the optically observed curves for various optical quantities;
- b) The theory when best fitted to the optical curves should reproduce various d.c. electrical and lattice parameters in satisfactory agreement with the measured values;
- c) In order to satisfy the correspondence requirement in the classical region, the theory should produce successfully the well known and time-tested classical formulae for various dispersion properties in the classical case of small $\hbar\omega$ or high temperature; and
- d) As another requirement of the correspondence it should be able to reproduce the well known temperature-dependence of various d.c. electrical and some thermodynamic properties in the limit of zero frequency or infinite wavelength.

None of the existing quantum mechanical theories succeed in satisfactorily meeting all four of these criteria. Some

salient features of the present theory shall be summarized itematically, and it is expected that this will also serve as comparison between the present theory and the existing theory.

In the present theory the quantum mechanical corrections to the classical dispersion formulae are mostly revealed in the frequency- and temperature-dependence in the over-all damping coefficient $\Gamma(\omega, T)$. $\Gamma(\omega, T)$ differs significantly from the corresponding d.c. value $\Gamma_0(T)$, which is the one used in the classical Drude and Hagen-Rubens theories, only in the spectral and temperature ranges where the quantum effects are important. This is conveniently represented by introducing the relation

$$\Gamma(\omega, T) = b(\omega, T) \Gamma_0(T) \quad \text{I-(1)}$$

where the b-factor is particularly important in the quantum mechanical region of high frequency and low temperature. Aside from the appearance of the b-factor, the present theory offers various optical and infrared dispersion formulae which bear very close resemblance to the well known classical formulae. Thus, it is clear that establishing the frequency- and temperature dependences of Γ or b will occupy the heart of the present theory. Results for non-transition metals apply mostly to those metals which have $\sim T^5$ -dependence on temperature of the electron-phonon part of the resistivity at

low temperature. The transition metals are shown to exhibit, in temperature- and frequency dependences, properties distinct from those of non-transition metals. The ferromagnetic and paramagnetic transition metals are investigated independently. It is found that the electron-phonon part of the dispersion formulae for transition metals for which the number of s-electrons is completely compensated by the number of empty states (positive holes) in the d-band, leads to $\sim T^3$ -dependence of d.c. resistivity, while the formulae for those transition metals in which the total number of S-electrons are not sufficient to close the d-band, lead to a negative exponential temperature-dependence at very low temperatures. There are further differences in temperature-dependences between ferromagnetic and paramagnetic transition metals which are offered by the theories of Weiss and, at low temperatures, of Heisenberg.

Generally, the over-all damping coefficient $\Gamma(\omega, T)$ is a sum of the contributions by the electron-phonon collisions, electron-electron collisions, and the impurity scattering such that

$$\Gamma(\omega, T) = \Gamma_{ep}(\omega, T) + \Gamma_{ee}(\omega, T) + \Gamma_M(T) \quad I-(2)$$

where the subscripts (ep), (ee) and (M) represent the three processes in the order mentioned above, and where the quantum correction factors, $b_{ep}(\omega, T)$ and $b_{ee}(\omega, T)$, may be defined for the first two processes in such a way that

$$\begin{aligned}
 \Gamma_{ep} &= \Gamma_{oep}(T)b_{ep}(\omega, T) \\
 \Gamma_{ee} &= \Gamma_{oee}(T)b_{ee}(\omega, T) \\
 b(\omega, T) &= \left(\frac{\Gamma_{oep}}{\Gamma_o} b_{ep}(\omega, T) + \frac{\Gamma_{oee}}{\Gamma_o} b_{ee}(\omega, T) + \frac{\Gamma_M}{\Gamma_o} \right)
 \end{aligned}
 \tag{I-3}$$

Among the three processes only the electron-phonon process is important at ordinary temperatures and in the free-electron region of the spectrum provided that the metal sample is a reasonably pure one. Many studies have been made on the contributions of the electron-electron collisions and the impurity scattering to optical and infrared absorption in metals.

Among the latest developments, the most prominent are the works of Pitaevskii, Silin and Gurzhi. According to these authors, the electron-electron collisions may contribute significantly either at very low temperatures or in the high frequency limit of the infrared spectrum, while the impurity scatterings are important at very low temperatures even for a reasonably clean sample. In particular, Gurzhi has derived a frequency-dependent electron-electron damping coefficient $\Gamma_{ee}(\omega, T)$ as well as a general formula for the impurity contribution to the damping.

In the present work, a variety of metals, all of which are supposed to be of very small impurity content, have been investigated as to the relative importance of the three mechanisms of damping in the high frequency region and also at low

temperatures. As the result of this investigation it is found that although the suggestion of Pitaevskii, Silin and Gurzhi may apply to some special cases of transition metals, it does not strictly apply to other metals in most of the quantum mechanical region of the free electron spectrum. In fact, the electron-phonon process or the Holstein mechanism alone, in the form that is derived in the present theory, explains quite successfully (viz., up to 2 ~ 5%) the low temperature (4.2°K) near infrared ($1\sim 1.5\mu$) absorptivity of all the metals for which experimental data are available.

The calculations on transition metals in the present theory suggest that the electron-electron collisions and impurity scatterings are particularly important for those transition metals, and similarly for other multivalent non-transition metals, in which the interband transitions require a non-zero momentum transfer. For a transition metal of this kind, only the phonons of energy larger than a certain non-zero value are effective in the transitions, and as the result of this the electron-phonon part of the low temperature resistivity has the previously mentioned negative exponential nature. This applies to all the transition metals whose s -electrons are not sufficient to close the d -band, and the low temperature resistivity is due mostly to the electron-electron collisions with the well known T^2 -dependence on temperature as well as to the temperature-

independent impurity scatterings (Restwiderstand). On the other hand, for those transition metals whose S-electrons are exactly compensated by the positive holes in the d-band such as the triad, Pt, Ni and Pd, the T^3 -dependence of the electron-phonon part plus the T^2 -dependence of the electron-electron collision term define the temperature-dependence of the low temperature resistivity to the extent of neglecting an additional T -dependence in the electron-phonon part. This is partly in contrast to the earlier concept that the electron-electron collisions make predominant contributions at low temperatures for all transition metals.

Strictly speaking, the T^2 -dependence is predominant in the transition metals other than the triad at temperatures smaller than the value given by

$$\Theta_E \cong \frac{\hbar U_L |k_d - k_s|}{K} : \begin{matrix} < \\ > \end{matrix} 10^\circ K \quad I-(4)$$

which is also the lower limit in the summation over the phonon states, where k_d , k_s are the Fermi momenta for the d- and s-bands, U_L is the longitudinal phase speed of sound and K is the Boltzman constant.

All the optical dispersion quantities including the optical conductivity $\sigma(\omega, T)$, the optical dielectric constant $\epsilon(\omega, T)$, and absorptivity $A(\omega, T)$ that are calculated in the present theory show not only good fit to the corresponding

experimental curves throughout the entire free-electron infrared spectrum, but also reproduce various d.c. electrical properties in excellent agreement with the directly measured values for a number of non-transition and transition metals. They also reproduce exactly the well known temperature-dependences of the d.c. electrical properties (hence, also of heat capacity and thermal conductivity) such as the famous Grüneisen formula $G\left(\frac{\Theta}{T}\right)$ for non-transition metals. The Grüneisen formula has long been known to describe temperature-dependence in excellent agreement with observations for T not too much larger than Θ .

It is pointed out, as the result of the present theory, that the quantum corrections represented by $b(\omega, T)$ -factor can also be significant in a relatively long wavelength region of the infrared, when $\hbar\omega \approx KT$. This is clearly illustrated in the formula for the reflectivity,

$$R(\omega, T) \approx 1 - 2\sqrt{\frac{\omega}{2\pi\sigma_{d.c.}(T)}} [b(\omega, T)]^{\frac{1}{2}} \quad \text{I-(5)}$$

which applies to the Hagen-Rubens limit of the spectrum or when $\omega^2 \ll \Gamma^2$, where the b -factor, although close to unity in this spectral range, is usually different from unity by a small fraction, and becomes essentially equal to unity when $\hbar\omega \ll KT$ in which case the formula is identically the well known and time-tested Hagen-Rubens formula. In this sense,

Formula (5) may be called the generalized Hagen-Rubens formula.

The present theory also enables us to estimate such lattice parameters as the electron density, the effective mass values of optical electrons, the Fermi energy, the upper edge of the d-band in a transition metal, and longitudinal phase speed of sound, etc. The heat capacity and thermal conduction properties also follow as by-products of the present theory. The impurity content can be estimated from low temperature optical data even for a sample with such a small impurity content as to be undetectable at ordinary temperatures.

The calculations for absorptivity at very low temperatures include both normal and superconducting metals. For the superconducting metals or below the superconducting transition temperature, the calculations are assisted by the theory of superconductivity of Bardeen, Cooper and Schrieffer. That Holstein's bulk absorption process might be important in a superconductor was suggested recently by Richards and Tinkham. The calculations in the present work are intended as a check on the said suggestion and to see whether the existing gap between the experimental absorptivity and the predictions of Mattis and Bardeen can be explained by Holstein's mechanism. It may be noted that the absorptivity for light quanta, $\hbar\omega$, smaller than the energy

gap (at $T = 0^\circ \text{K}$) has been given by Schrieffer and has been shown to agree well with experiments. At the present no definite conclusion can be provided on the basis of the present calculations because of insufficient experimental data.

Finally, some words need to be said regarding possible limitations in the present theory. The limitations may result mainly from two causes: firstly, the use of the simple Debye model and secondly, the assumption of spherical Fermi surfaces.

The first assumption leads to difficulties at very high temperatures ($T \gg \Theta$) where the Umklapp process is important. The same difficulty is found in Gruneisen's formula for d.c. resistivity at very high temperatures.

Another less serious aspect of limitations in the use of the Debye model is in neglecting the anisotropy among the longitudinal and two transverse directions, whereas in more accurate calculations, one needs to consider three components of the phase velocity of sound as well as three characteristic temperatures instead of the Debye temperature alone. This problem of lattice anisotropy is of no concern for a polycrystalline metal sample. Perhaps the best

justification for using the simple Debye model is in the good agreement found between the theoretical and experimental values of heat capacity.

It is well known that the Umklapp processes are important at very low temperatures, especially for those metals in which the interband transitions are important. At very low temperatures, the Umklapp processes enter into various physical quantities through electron-electron collision terms and do not enter into the electron-phonon processes, since the angular deflection involved in an electron-phonon scattering is in the order of $\left(\frac{T}{\Theta}\right)$ which is certainly much less than unity. It is known that contribution by electron-electron collisions to the over-all damping coefficient vanishes when Umklapp processes are not present. In short, at very low temperatures, the Umklapp processes are important to the extent that the electron-electron collisions are important, and hence are automatically taken into consideration in the present theory by incorporating the effects of electron-electron collisions into various dispersion formulae.

The limitations that are associated with the assumption of a spherical Fermi surface are well known, and are often discussed in the literature. In general, this approximation works well for most monovalent metals such as the noble metals Ag, Au, and Cu, and also for some multivalent metals for which

the interband transitions are not important. On the other hand, the assumption of a spherical Fermi surface is not strictly valid for those non-transition metals in which the Fermi surface touches or almost touches the plane of energy discontinuity and for all transition metals in which the interband transitions between the s-and d-bands are most important. In the present theory, the calculations for non-transition metals are carried out on the basis of a spherical Fermi surface, while non-spherical Fermi surfaces have been used for all transition metals. Therefore, it is expected that the results on non-transition metals will not apply strictly to some multivalent metals.

The present work does not include detailed study of the optical and electrical properties of alloys, and also of such other properties of metals as thermoelectricity and magneto-resistive effects. Much has yet to be learned theoretically about the d.c. electrical properties before it is possible to study rigorously the optical and infrared dispersion properties of alloys.

An attempt has been made to make this thesis self-contained, but in view of all the relevant work yet to be done in the field of interest this was impossible. Similarly, an honest effort to give all due credit was made, but it is likely that some work has not been properly cited, such omissions were not intentional.

Chapter II

Fundamental Relations Between Optical And Electrical Properties Of Metals

II-A Maxwell's Equations and Kramers-Kronig Relation

Maxwell's theory of electromagnetism provides us with a set of the most fundamental relations between the optical properties and the electrical properties of metals. These relations plus the well known Kramers-Kronig relations between the real and imaginary parts of the complex polarizability constitute a foundation upon which the interpretation of the optical and infrared behavior of metals in terms of electrical properties is based.

If \underline{E} and \underline{H} are the electric and magnetic fields represented as functions of the coordinate \underline{r} and time t for a given angular frequency

$$\omega = [2\pi\nu \text{ sec.}^{-1}]$$

Maxwell's equations for an uncharged conductor are given in c.g.s. units by

$$\nabla \times \underline{H} = \frac{\epsilon}{c} \frac{\partial \underline{E}}{\partial t} + \frac{4\pi\sigma(\omega)}{c} \underline{E} \quad \text{II-(1)}$$

$$\nabla \times \underline{E} = \frac{\mu}{c} \frac{\partial \underline{H}}{\partial t} \quad \text{II-(2)}$$

$$\nabla \cdot \underline{E} = \nabla \cdot \underline{H} = 0 \quad \text{II-(3)}$$

where $\epsilon(\omega)$ is the real dielectric constant, $\sigma(\omega)$ is the conductivity, and μ is the permeability.

At optical and infrared frequencies, $\mu = 1$ for all substances. The magnetic field \underline{H} is eliminated by combining Equations (1) and (2) and we obtain

$$c^2 \nabla^2 \underline{E} = \epsilon \frac{\partial^2 \underline{E}}{\partial t^2} + 4\pi\sigma \frac{\partial \underline{E}}{\partial t} \quad \text{II-(4)}$$

The solution to this differential equation is given by the typical solution to the usual wave equation,

$$\underline{E} = \underline{E}_0 e^{i\omega t \pm i(\epsilon\omega^2 - i4\pi\sigma\omega)^{-\frac{1}{2}} z/c} \quad \text{II-(5)}$$

where \underline{E}_0 is the maximum amplitude (i.e., at $z = 0$, $t=0$) and z measures the penetration distance into the metal. The solution (5) takes on the conventional form expressed in terms of the complex index of refraction \bar{N} ,

$$\underline{E} = \underline{E}_0 e^{i\omega(t \pm \bar{N} \frac{z}{c})} \quad \text{II-(6)}$$

if we identify \bar{N} with $[...]^{\frac{1}{2}} \omega^{-1}$ of Equation (5):

$$\bar{N} = (n-ik) = [\epsilon - i \frac{4\pi\sigma}{\omega}]^{\frac{1}{2}} \quad \text{II-(7)}$$

where n and k represent the index of refraction and absorption coefficient, respectively.

The relation (7) immediately yields the following two important relations between the electric properties

$[\sigma(\omega), \epsilon(\omega)]$ and optical constants (n, k) :

$$\epsilon = n^2 - k^2 \quad \text{II-(8)}$$

$$\sigma = nk\omega/2\pi \quad \text{II-(9)}$$

These two relations will be referred to frequently.

The physical significance of $\sigma(\omega)$ for $\omega > 0$ becomes evident when we calculate the rate of energy loss by computing the Poynting vector \underline{S} ,

$$\underline{S} = \frac{c}{4\pi} (\underline{E} \times \underline{H}) \quad \text{II-(10)}$$

and taking the time average of

$$-W = \frac{\partial S_z}{\partial z}$$

where W is the Joule heat produced per unit time and per unit volume within the conducting medium. Then, we obtain as the definition of $\sigma(\omega)$

$$\sigma(\omega) = \bar{W} / \frac{E^2}{2} \quad \text{II-(11)}$$

which says that σ is the fraction of the energy absorbed or dissipated per unit time and unit volume out of the energy density per unit volume $\frac{E^2}{2}$, of the electromagnetic field of frequency ω . It is quite obvious then that $\sigma(0)$, at $\omega = 0$, should be the d.c. conductivity of the metal. It

is a popular practice to introduce a complex dielectric constant $\bar{\epsilon}$ and complex polarizability $\bar{\alpha}$ such that

$$\bar{\epsilon} = 1 + 4\pi\bar{\alpha} = \bar{N}^2 \quad \text{II-(12)}$$

$$\bar{\alpha} = \alpha - i\alpha' \quad \text{II-(13)}$$

This is analogous to the similar relation for the real quantities,

$$\epsilon = 1 + 4\pi\alpha = n^2 - k^2; \mu = 1 \quad \text{II-(14)}$$

Then, upon comparing Equations (12) and (13) with Equation (7), we now have

$$\epsilon = 1 + 4\pi\alpha = n^2 - k^2 \quad \text{II-(15)}$$

$$4\pi\alpha' = \frac{4\pi\sigma}{\omega} = 2nk \quad \text{II-(16)}$$

These two relations enable us to obtain (n,k) values upon knowing the values of the dielectric constant ϵ and conductivity σ at a given frequency, and, conversely, to obtain ϵ and σ values from known values of n and k. In general, the observations in the optical and infrared part of the spectrum are designed to measure the optical constants (n,k) or other optical properties such as the reflectivity and emissivity (= absorptivity for metals). Therefore, for the purpose of predicting (n,k) values for a given frequency

ω and temperature T ($^{\circ}\text{K}$) from a known set of values of the d.c. electric properties $\epsilon(0)$ and $\sigma(0)$, or for the purpose of predicting the d.c. electric properties from measured values of (n,k) , we need to have a set of theoretical equations relating $\epsilon(\omega)$ and $\sigma(\omega)$ to the corresponding d.c. quantities $\epsilon(0)$ and $\sigma(0)$. Specifically, the frequency and temperature dependence of $\sigma(\omega)$ and $\epsilon(\omega)$ needs to be specified.

Establishing the correct ω - and T -dependence of σ and ϵ constitutes a major part of the theoretical work explaining the optical, infrared, and the related electrical properties of metals. Fortunately, the solution to the theoretical problem is considerably simplified with the aid of the Kramers-Kronig relation which represents an integral relation between $\sigma(\omega)$ and $\epsilon(\omega)$, or, more properly, between the real and imaginary parts of the complex polarizability as follows:

$$\frac{1}{2}\alpha(\omega) = - \frac{P}{\pi} \int_0^{\infty} \frac{\omega' \alpha'(\omega')}{\omega'^2 - \omega^2} d\omega' \quad \text{II-(17)}$$

With the help of Equation (16), this represents a relationship between $\epsilon(\omega)$ and $\sigma(\omega)$ given by

$$\frac{[\epsilon(\omega)-1]}{4\pi} = - \frac{P}{\pi} \int_0^{\infty} \frac{d\omega' \sigma(\omega')}{(\omega'^2 - \omega^2)} \quad \text{II-(18)}$$

Therefore, it is sufficient to specify the ω - and T -dependence of either σ or ϵ for establishing the complete ω - and T -dependent structure of the optical and electrical

quantities that are involved in Equations (15) and (16).

In a more general discussion of the Kramers-Kronig relation, Equations (17) and (18) are equivalently represented in the form

$$\operatorname{Re} [\bar{N}(\omega) - 1] = \frac{P}{\pi} \int_{-\infty}^{+\infty} d\omega' \frac{\operatorname{Im} [\bar{N}(\omega') - 1]}{\omega' - \omega} \quad \text{II-(19)}$$

which may be recognized as the real part of the equation

$$[\bar{N}(\omega) - 1] = \frac{1}{i\pi} P \int_{-\infty}^{+\infty} d\omega' \frac{[\bar{N}(\omega') - 1]}{\omega' - \omega} \quad \text{II-(20)}$$

or in the limit of $\eta \rightarrow 0^+$

$$[\bar{N}(\omega) - 1] = \frac{1}{2\pi i} \int_{-\infty}^{+\infty} d\omega' \frac{[\bar{N}(\omega') - 1]}{\omega' - (\omega + i\eta)} \quad \text{II-(21)}$$

Equation (20), which is the most general representation of the Kramers-Kronig relation, was observed by Kramers as a simple consequence of Cauchy's theorem if we assume that $\bar{N}(\omega)$ is a function of a complex variable ω analytic in the upper half ω -plane which approaches unity at infinity. It was later shown by Kronig that the absence of poles of $\bar{N}(\omega)$ in the upper half ω -plane was both a necessary and sufficient condition for the property that no signal may propagate through a medium with index of refraction $\bar{N}(\omega)$ with a speed greater than that of light.

Sometimes, the optical properties of a medium are expressed in terms of the forward scattering amplitude $F(\omega)$ and the total scattering cross-section per scattering center $\sigma_s(\omega)$ rather than in terms of (α, σ) or (n, k) .

The equation which shows the relation between the complex forward scattering amplitude $\bar{F}(\omega)$ and the complex index of refraction $\bar{N}(\omega)$ was first offered by Lorentz, namely,

$$[\bar{N}(\omega) - 1] = n_0 \frac{2\pi c^2}{\omega^2} \bar{F}(\omega) \quad \text{II-(22)}$$

where n_0 is the number of scattering centers per unit volume. The same derivation leading to Equation (22) also yields the optical theorem

$$\sigma_s(\omega) = 4\pi c \operatorname{Im}\left(\frac{\bar{F}(\omega)}{\omega}\right) \quad \text{II-(23)}$$

where $\sigma_s(\omega)$ is the total cross-section in cm^2 per scatterer. The above relation also follows very simply upon noting that the intensity of a wave propagating through a medium of refractive index $\bar{N}(\omega)$ is reduced in a distance z by a factor $|\exp[i \frac{\omega}{2} \bar{N}(\omega) z]|^2$ and also by $e^{-n_0 \sigma_s(\omega) z}$ according to the definition of $\sigma_s(\omega)$. Comparison of these two expressions gives Equation (23).

Upon comparing Equations (22) and (23) with the relations (12) ~ (16), some useful relations follow.

We have, for instance,

$$n(\omega) = \text{Re} \bar{N}(\omega) = 1 + \frac{2\pi n_0 c^2}{\omega^2} \text{Re} \bar{F}(\omega) \quad \text{II-(24)}$$

$$\begin{aligned} k(\omega) &= -\text{Im} \bar{N}(\omega) = -\frac{2\pi n_0 c^2}{\omega^2} \text{Im} \bar{F}(\omega) \\ &= -\frac{n_0 c}{2\omega} \sigma_s(\omega) \end{aligned} \quad \text{II-(25)}$$

$$\epsilon(\omega) = \text{Re} \cdot \bar{N}^2 = (1 + 4\pi\alpha)$$

$$= \left[\left(1 + \frac{2\pi n_0 c^2}{\omega^2} \text{Re} \bar{F}(\omega) \right)^2 - \left(\frac{2\pi n_0 c^2}{\omega^2} \text{Im} \bar{F}(\omega) \right)^2 \right] \quad \text{II-(26)}$$

$$\sigma(\omega) = -\frac{\omega}{4\pi} \text{Im} \cdot \bar{N}^2 = \omega\alpha'$$

$$= -\frac{n_0 c^2}{\omega} \left(\text{Im} \cdot \bar{F}(\omega) \right) \left(1 + \frac{2\pi n_0 c^2}{\omega^2} \text{Re} \cdot \bar{F}(\omega) \right) \quad \text{II-(27)}$$

where the real and imaginary parts of $\bar{F}(\omega)$ are related to each other through Kramers-Kronig relation

$$\begin{aligned} \text{Re} \bar{F}(\omega) &= \frac{\omega^2}{\pi} \text{P} \int_{-\infty}^{+\infty} d\omega' \frac{\text{Im} \bar{F}(\omega')}{\omega'^2 (\omega' - \omega)} \\ &= \frac{2\omega^2}{\pi} \text{P} \int_0^{\infty} d\omega' \frac{\text{Im} \bar{F}(\omega')}{\omega' (\omega'^2 - \omega^2)} \end{aligned} \quad \text{II-(28)}$$

In applying the relations (24) ~ (27) to the infrared dispersion in metals, we need only to remember that n_0 is the effective number of conduction electrons per cm^3 and that $\sigma_s(\omega)$ is the total scattering cross-section for the conduction electron - external photon interactions including the absorption, emission, and the scattering in the ordinary sense.

II-B Absorptivity (Emissivity) and Reflectivity

Various optical, infrared and electrical properties may be obtained from measurements of the absorptivity (A) and reflectivity (R), as well as from n and k . The two quantities are related by the equation,

$$R = 1 - A \quad \text{II-(29)}$$

The relationship between (R,A) and the electrical properties will follow naturally from Equations (15) and (16), when we establish the relationship between (R,A) and (n,k).

The optical theory gives the well known result that for normal incidence

$$R = \left| \frac{\bar{N} - 1}{\bar{N} + 1} \right|^2 = 1 - A \quad \text{II-(30)}$$

which defines the reflectivity and absorptivity in terms

of the complex index of refraction $\bar{N} = n - ik$. In particular, for a transparent medium such as glass, we have $\bar{N} = n$, and Equation (30) gives the well known formula

$$R = \left(\frac{n-1}{n+1} \right)^2$$

Equation (30) completely determines R and A in terms of n and k. In order to express R and A in terms of σ and ϵ , it is convenient to follow the simple algebraic method of Price (1949) rather than to use Equations (15) and (16). Upon writing, for the complex polarizability, $\bar{\alpha}$

$$[4\pi\bar{\alpha}]^{-1} = (x + iy) \quad \text{II-(31)}$$

The absorptivity is given by

$$\frac{A^2}{8R} = \frac{A^2}{8(1-A)} = T + (T^2 + Y^2)^{\frac{1}{2}} \quad \text{II-(32)}$$

where

$$\begin{aligned} T &= x + x^2 + y^2 \\ 1 - \epsilon &= 1 + k^2 - n^2 = x/x^2 + y^2 \\ \frac{4\pi\sigma}{\omega} &= 2nk = -y/x^2 + y^2 \end{aligned} \quad \text{II-(33)}$$

and these are just as well represented in terms of the real and imaginary parts of scattering amplitudes according to the relations (24) ~ (27).

The frequency- and temperature-dependence of R and A will then be determined when the ω - and T-dependent structure of σ or ϵ is obtained theoretically. The spectral and temperature variation of R and A will vary depending on the choice of the particular theoretical model used in calculating the complex polarizability. In particular, if we adopt the classical free electron theory of Drude (1904, 1902), the real and imaginary parts of the complex polarizability are given by

$$\begin{aligned}x &= - (\omega \tau_o)^2 \\y &= - (\omega \tau_R)^2\end{aligned}\tag{II-34}$$

where

$$\tau_o = \sqrt{\frac{m^*}{4\pi n_o e^2}}$$

$$\tau_R = \Gamma_o^{-1} \quad = \text{the relaxation time of a conduction electron}$$

$$m^* \quad = \text{the effective mass of a conduction electron}$$

$$e \quad = \text{the electronic charge} \\ (= 4.8 \times 10^{-10} \text{ e.s.u.})$$

$$n_o \quad = \text{the effective number of conduction electrons per unit volume}$$

Price (1949) presents an extensive investigation on the qualitative features of the spectral and temperature

variations of A and R for metals to which one electron dispersion theory can be applied in the form of Equation (24).

In general, the expressions for x and y will assume different forms for different theoretical models. A brief review on some of the most popular theories on optical and infrared dispersion is presented in the chapter that follows.

Chapter III

Existing Theories on Optical and Infrared Dispersion in Metals

III-A Hagen-Rubens Theory

Theoretical discussions on the behavior of metallic conductors under the influence of electromagnetic waves were first given by Hagen and Rubens (1903) and by Drude (1904) on the basis of classical electrodynamics.

The Hagen-Rubens theory is restricted in its applicability to the long wavelength part of the spectrum where $(\omega \tau_R)^2$ is much smaller than unity, τ_R being the relaxation time characteristic of the damping in the electronic motion. The results of the Hagen-Rubens theory follow from Equation II-(8), (9), and (20) upon taking

$$\sigma(\omega) \cong \sigma(0) = \sigma_{d.c.} \quad \text{III-(1)}$$

in the long wavelength part of the spectrum. We thus have

$$nk \approx \left(\sigma_{d.c.} / \nu \right) \quad \text{III-(2)}$$

It may be shown that $\left(\sigma_{d.c.} / \nu \right)$ is much larger than unity for the wavelengths for which the approximation (1) is valid, and hence, approximately

$$n \cong k \cong \sqrt{\frac{\sigma_{d.c.}}{\nu}} \quad \text{III-(3)}$$

$$R = 1-A \approx 1-2 \sqrt{\frac{\nu}{\sigma_{d.c.}}} \quad \text{III-(4)}$$

where the latter expression is obtained upon substituting (3) into II-(20). The formula (4), which is known as the Hagen-Rubens relation, has been compared with the experiment for infrared radiation and for various metals and temperatures (Hagen and Rubens, 1903), and it is in general in fair agreement with the experiment for

$$\lambda \gtrsim 10 \mu$$

The approximation represented by (1) is equivalent to taking the current \underline{J} in phase with the applied electric field \underline{E} . This will be true only if the relaxation time τ_R of the electron is small compared with the period of the light wave so that the field acting on the electron is approximately constant during the time taken by an electron to traverse its mean free path. For wavelengths shorter than $\sim 10 \mu$, the current will be out of phase with the field, and it is generally observed that the formula (3), (4), and (2) are not even approximately in agreement with the experiment.

III-B Drude Theory

A more general theory than that of Hagen and Rubens was given by Drude (1904) by obtaining the solutions to the classical equation of motion for free conduction electrons subject to Maxwell's electromagnetic field.

In contrast to the Lorentz theory (Lorentz 1906) of absorption by dielectrics, which rests on the assumption that bound charges become polarized upon interaction with the electromagnetic wave, Drude (1902, 1904) suggested that the optical properties of metals could be explained by consideration of the interaction between the free conduction electrons in the metal and electromagnetic wave. The solution for the conductivity $\sigma(\omega)$ is obtained upon solving the equation

$$m^* \ddot{\underline{s}} + m^* \Gamma_0 \dot{\underline{s}} = -e \underline{E}_0 e^{-i\omega t} \quad \text{III-(5)}$$

where \underline{s} is the electron position coordinate within the metal, $\underline{E} = \underline{E}_0 e^{-i\omega t}$ is the applied electromagnetic field, and Γ_0 is the damping coefficient which is also equal to the inverse of the d.c. relaxation time τ_R . Using the effective mass m^* in Equation (5) instead of the normal electron mass m which was used in the original Drude theory (1904), we have incorporated the later developed effective mass method with the primitive free electron theory of Drude.

Equation (5) yields the expressions for the conductivity $\sigma(\omega)$ and the dielectric constant $\epsilon(\omega)$,

$$\sigma(\omega) = \frac{nk\omega}{2\pi} = \frac{\sigma(0)}{1 + (\omega\tau_R)^2} \quad \text{III-(6)}$$

$$[1 - \epsilon(\omega)] = 1 + k^2 - n^2 = \frac{4\pi\sigma(0)\tau_R}{1 + (\omega\tau_R)^2} \quad \text{III-(7)}$$

where we used the notations,

$$\tau_R = \Gamma^{-1}$$

$$\sigma(0) = \frac{ne^2}{m^*} \bigg/ \Gamma_0 \quad \text{III-(8)}$$

We see that

$$\sigma(\omega) \underset{\omega \rightarrow 0}{\sim} \sigma(0) \quad \text{III-(9)}$$

so that $\sigma(0)$ is the d.c. conductivity.

It can be shown readily that the relations (6) and (7) reduce to the simple relations (2), (3) and (4) of the Hagen-Rubens theory in the limit

$$(\omega\tau_R)^2 \ll 1$$

On the other hand, the results of the Drude theory do not apply to that part of the short wavelength region where the contribution of the bound electrons enter (i.e.,

the resonance region) through the photo-electric effects. At the shorter wavelengths, the anomalous dispersion occurs due to the contributions of the photo-electric absorption, and also the core polarization becomes important. In this part of the spectrum, the simple free electron theory of Drude is not enough to explain the observed dispersion, and will be modified, for the dielectric constant, as follows:

$$(\epsilon-1) = n^2 - k^2 - 1 = -\frac{4\pi n_e e^2}{m^* \omega^2} + (\epsilon-1)_c + (\epsilon-1)_p \quad \text{III-(10)}$$

where $(\epsilon-1)_c$ is the contribution of the core polarization and $(\epsilon-1)_p$ of the photoelectric absorption.

In general, the anomalous dispersion is observed at a wavelength well below $\sim 1\mu$. Ag, Au, and Cu, for instance, have their lowest resonances at 0.27μ , 0.37μ , and 0.50μ (Meier, 1910), respectively. As long as one stays at wavelengths which are long enough to be sufficiently outside the resonance tail, the free electron theory of Drude should be satisfactory. At the high frequency region where the condition

$$(\omega \tau_R)^2 \gg 1$$

is satisfied, the free electron part of $\sigma(\omega)$ and $\epsilon(\omega)$ are given by

$$\sigma(\omega) \approx \sigma(0) / (\omega \tau_R)^2$$

$$\epsilon - 1 \approx - \frac{4\pi n_e e^2}{m^* \omega^2}$$
III-(11)

The values of $(\epsilon - 1)_c$ are available for a variety of metals (Van Vleck, 1959), and are generally independent of frequency (Mott and Jones, 1936). The value of $(\epsilon - 1)_p$ may be found either by a direct theoretical calculation, or empirically from the observed data of (n, k) values. The photoelectric part $(nk)_p$ of the observed (n, k) values is obtained empirically upon subtracting the free electron part (i.e., the Drude part) from the observed (n, k) values making use of the relation (11). Then, $(\epsilon - 1)_p$ is obtained, in turn, upon making use of the Kramers-Kronig relation II-(18),

$$(\epsilon - 1)_p = \frac{4}{\pi} \int (nk)_p \frac{\omega' d\omega'}{\omega'^2 - \omega^2}$$
III-(12)

For wavelengths sufficiently outside the photoelectric region, $(\epsilon - 1)_c$ and $(\epsilon - 1)_p$ are small enough to be neglected compared with the free electron part. We shall be primarily interested in this part of the spectrum where only the free conduction electrons play a dominant role.

Equations (6) and (7) show that the two Drude equations are related with each other by a rather simple algebraic relation,

$$\sigma/1 - \epsilon = (4\pi\tau_R)^{-1} = \Gamma_0/4\pi = nk\nu/1 + k^2 - n^2 \quad \text{III-(13)}$$

This relation enables us to obtain the value of the d.c. damping coefficient Γ_0 or the d.c. relaxation time τ_R when we have only one pair of (n,k) values at an arbitrary frequency, provided that the frequency ω is not too large.

A more exact way of determining the value of Γ_0 would be to plot $\sigma(\omega)$ against $(1-\epsilon)$ from a set of (n,k) values, and then determine the slope $(\Gamma_0/4\pi)$ of the resulting straight line. This method was first pointed out by Wolfe (1954, 1955). Any deviation of the curve from the Drude straight line would also provide us with a measure of the validity of the Drude theory at a given frequency.

Beattie and Conn (1955) plotted the Argand diagrams showing $(2nk/\lambda)$ against $(n^2 - k^2)$ for Al, Ag, Ni and Cu. The values of Γ_0 and τ_R determined from the slopes vary greatly depending on the way the metal surfaces are prepared. The best agreements of the d.c. conductivity values σ_0 which are obtained upon substituting the Γ_0 values into

the Drude equation (6), with the electrically measured values were obtained for evaporated metal films. The results of Beattie and Conn are presented in Table 1. The discrepancy between the measured and calculated (Drude Theory) values of the d.c. conductivity for evaporated films of Ag, Cu, Ni and Al are found as 40%, 100%, 40 ~ 50%, and 40% respectively. The calculated values are always smaller than the measured values. These results will be further discussed in a later chapter, and it will be shown that the mentioned discrepancy can be explained theoretically upon introducing an additional frequency-dependent factor into the original Drude equation.

For none of the metals that were studied by Beattie and Conn (1955) did the Argand diagrams yield complete straight lines. For Al, for instance, the curve starts to deviate from the straight line at $\sim 8\mu$. The deviation becomes more pronounced toward the shorter wavelengths as one might have expected. An interesting feature is that the Argand diagrams start to deviate from a straight line long before the wavelength enters the photoelectric resonance tail.

With almost no exception, the d.c. conductivity σ_0 calculated according to the Drude Theory from the observed values of optical constants is always smaller than the

measured value even when very carefully prepared metal surfaces are used. Thus, it seems that the classical free electron theory of Drude contains some basic limitations.

Of all the existing theories on the optical and infrared dispersion in metals, the classical free electron theory of Drude (1904, 1902) has been most successful in explaining the experimental results aside from some exceptional cases that will be discussed later.

The Drude Theory has been applied to a large number of metals with varying degrees of success. An excellent review by Schulz (1957-a) and the review by Blau et al (1958) gives a detailed account of this work as well as references to many of the original papers. The basis for the relative success of the Drude Theory lies in the fact that, for a number of metals for which sufficient data on (n,k) values are available, Equations (6) and (7) can be fitted to the optically determined curves of $\sigma(\omega)$ and $[1-\epsilon(\omega)]$ upon adjusting Γ_0 and $\sigma(0)$ or n_e and m^* to suitable values (Schulz, 1957-a,b,c, 1951, 1954; Beattie and Conn, 1955; Seitz and Turnbull, 1958 and others).

For Au, Ag and Cu, which have their first resonances at 0.37μ , 0.27μ , and 0.5μ , respectively (Meier, 1910), the Drude Equations (6) and (7) can be fitted to the experimental curves with $m^*(Cu) = 1.45m$, and $m^*(Au) = m^*(Ag) = m$

TABLE I

	I	II	
Metal	$\sigma_o \times 10^{-16}$ e.s.u. (calc)	$\sigma_d \times 10^{-16}$ e.s.u. (measured)	$\frac{\sigma_{II}}{\sigma_I}$
Al	11.6	15.0	1.3
Ni	$\begin{pmatrix} 3.16 \\ 1.02 \end{pmatrix}$	$\begin{pmatrix} 4.6 \\ 1.4 \end{pmatrix}$	$\begin{pmatrix} 1.5 \\ 1.4 \end{pmatrix}$

for $\lambda \geq 2\mu$ (Schulz, 1957-a). The optical behavior of the three simple monovalent metals is clearly consistent with the Drude theory at least so far as the frequency dependence is concerned.

Another example of excellent agreement between theory and experiment is found in the liquid metals Hg and Ga (Schulz, 1957-b). For these metals, the theory fits well for $\lambda \gtrsim 0.3\mu$.

Except for the case of the liquid metals, the success of the Drude theory mentioned above is no more than a qualitative one. For the theory to be quantitatively consistent, the values of the electric properties such as $\sigma(0)$ and $\epsilon(0)$ as well as other lattice parameters must agree with the measured values when calculated from the measured optical constants. And conversely, the optical constants calculated from the measured values of $\sigma(0)$ and $\epsilon(0)$ should agree with the measured values of the optical constants. However, in practically all cases that have been studied, the d.c. conductivity values calculated from the best-fit Drude curves are found to be smaller than the handbook values, for monovalent as well as multivalent metals. Such discrepancies occur sometimes by a factor of $2 \sim 10$ (see, for instance, Seitz and Turnbull, 1958; Beattie and Conn, 1955).

As it was shown by Beattie and Conn (1955), the d.c. conductivity calculated according to the Drude theory from

the measured values of optical constants depends very strongly on the manner in which the metal surface is prepared. The discrepancy was smallest, being of the order of 40 ~ 100 percent, for the case of evaporated metal films, while for metals prepared in other ways the calculated d.c. conductivity values were smaller than the handbook values by a large factor of 3 ~ 5. Although the large discrepancies in the case where the surfaces are prepared by a method other than by evaporation may be explained as arising from the crystal structure of the metal surface being disturbed during the process of polishing such as introducing an amorphous layer, the discrepancy for the case of evaporated films is yet to be explained. The only cases where both qualitative and quantitative agreements are found are the liquid metals Hg and Ga.

In general, the agreement between the theory and experiment for solid, multivalent metals is more incomplete than for monovalent metals such as gold, silver and copper. At best, a partial agreement over a narrow spectral region can be obtained through suitable adjustment of the parameters n_e , m^* , and $\sigma(0)$. This procedure for multivalent metal is justified, as will be explained , when the contribution to $\sigma(\omega)$ and $\epsilon(\omega)$ of one band is predominant over the second band contribution in a certain range of the spectrum in the two-band description of the free electron

theory. In this range of the spectrum, the metal may be treated effectively with the one-electron formula of Drude. By adjusting n_e and $\sigma(0)$, Hodgson (1955) was able to fit measured values of n and k for the divalent metal Zn from 2 to 15 μ . The value of n_e was substantially lower than that calculated, and the value of $\sigma(0)$ substantially lower than that measured. For the trivalent metal Al, Hodgson (1955) and Beattie (1955) could fit the Drude curves to the optical curves in the spectral range of 1 ~ 10 μ , using suitably reduced values of n_e and $\sigma(0)$.

In spite of the good agreement found in the liquid metals Hg and Ga, it was found (Schulz, 1957-c) that the liquid alloys Hg-In, Hg-Tl, and Ga-In are in complete disagreement with the theory. This is in contrast to the earlier studies of Kent (1919) which pointed out that some liquid alloys follow the Drude theory. But these studies were confined to a very short wavelength range. Some of the early studies on the optical properties of liquid metals (Kent, 1919), bismuth, lead, cadmium and tin, in the spectral range of 0.404 μ to 0.579 μ shows a remarkable agreement with the Drude theory as shown in Table III.

III-C Electron-Lattice Interaction and Anomalous Skin Effects

In the original theory of Drude (1904), the viscous damping coefficient Γ_0 was used without specific reference to the physical mechanism giving rise to the damping. The introduction of Γ_0 was necessary in order to maintain a consistency between the electromagnetic dispersion and the finite d.c. resistivity on the basis of the free electron model. In this sense, the damping coefficient was used as a parameter whose magnitude was to be determined either from the measured electrical properties or from the measured optical data. Kronig (1927) reconsidered the problem in the frame of the modern theory of metals, showing that if the conduction electrons are treated as moving in a periodic potential perturbed by the thermal agitation of the lattice, they can be held responsible for the optical properties in the infrared as well as for the characteristic absorption and refraction in the visible and near ultraviolet parts of the spectrum. In other words, Kronig attributed the occurrence of finite Γ_0 to the mechanism of the electron-lattice interaction.

The mechanism of the electron-Lattice interaction or the electron-phonon interaction as it is popularly interpreted in modern theory, and of impurity scattering when the metal contains a substantial amount of impurities, has shown enormous success in explaining various physical

TABLE III

LIQUID METALS

Metal	Bi	Pb	Cd	Sn	Hg
Ne/atom (calculated)	5.1	5.1	2.4	4.1	2.1
$1/\sigma_0$ (μ ohm/cm) calculated	128	94	33.4	54	87.3
$1/\sigma_{dc}$ (μ ohm/cm) measured	134	98	34	52	94

qualities of metals such as the thermal and electric conduction, the Wiedemann-Franz law, the Matthiessen rule, the dependence of the electric resistance on temperature and pressure, and many others. (See, for instance, Wilson, 1936 and Mott and Jones, 1936.)

The impurity scattering introduces a residual resistance (Restwiderstand) and represents the temperature-independent, additive quantity of resistivity in the Matthiessen rule. A further progress on the behavior of metallic conductors under the influence of electromagnetic waves was made by Reuter and Sondheimer (1948) and was later elaborated by Dingle (1953), Gordon and Sondheimer (1953) and Pitaevski (1958). This work concerns the phenomenon that is popularly referred to as the anomalous skin effect and is important only at low temperatures.

Reuter and Sondheimer (1948), following a suggestion of London (1940), investigated the case, important at low temperatures, that the mean free path of the conduction electrons for collisions with the lattice is of the same order of magnitudes as, or even large, compared with the normal penetration depth (skin depth) of the electromagnetic waves in the metal. In this case, the way in which the metal boundary influences the motion of the electrons arriving there becomes important. The authors distinguished two extreme cases: namely, that of the specular reflection

at the surface and that of completely diffuse reflection, the latter being at least approximately realized in nature according to the available evidence. Dingle (1952, 1953) added elaboration to the original theory of Reuter and Sondheimer, and showed, in particular, that, especially in the case of diffuse reflection, the values resulting for the absorptivity $A(=1-R)$ of the metallic surface may differ widely from the predictions of standard theory. Qualitatively, this is to say that in this case the loss of momentum parallel to the boundary, which an electron suffers when diffusely reflected by it, furnishes a contribution to the real part of the surface impedance of the metal. This contribution remains even if, by lowering the temperature, the bulk resistivity and with it the energy loss in the interior of the metal are reduced. Hence, the metal still retains a non-zero absorptivity when the bulk resistivity is made to vanish by lowering the temperature to 0°K . This conclusion was qualitatively predicted by the experiments of Ramanathan (1952) at the liquid helium temperature. The success of the theory of anomalous skin effect in accounting for the reflectivity of metals has been conclusively demonstrated by Dingle (1953) and Pitaevski (1958).

In its present state of development, the theory of the anomalous skin effect applies strictly to the alkali metals

and monovalent metals such as Au, Ag, and Cu. Like the simple Drude theory, the anomalous skin effect does not apply in a region of strong resonance absorption. Table II shows the values of the absorptivity A,

$$A = A_v + A_s \quad \text{III-(14)}$$

for Cu and Ag, where A_s is the diffuse skin absorptivity

$$A_s = \frac{3}{4} \left(\frac{V_f}{c} \right) \quad \text{III-(15)}$$

V_f being the Fermi velocity of electron and c the speed of light, and A_v is the bulk contribution to the absorption resulting primarily from the electron-phonon interactions. The values of A_v for Cu and Ag have been obtained from the formula that will be derived in the calculations of Chapter IV. It is seen in Table II that the bulk and skin effects added together show agreements with the experimental values up to about 2 percent.

Associated with the skin effect is the skin depth which is the thickness at the metal surface in which most of the optical skin effect is observed, and is given by

$$\delta_s = \left(\frac{m^* c^2}{4\pi n_0 e^2} \right)^{\frac{1}{2}} \quad \text{III-(16)}$$

and is in the order of several thousand angstroms. This is not to be confused with the so-called penetration depth

δ_p which is a distance characteristic of the surface penetration by light of given wavelength and is the distance at which the intensity falls to $\frac{1}{e}$ of that at the surface. It is given by

$$\delta_I = \frac{\lambda}{4\pi k} \quad \text{III-(17)}$$

where k is the absorption index. For sodium at $\lambda = 0.6\mu$, $k = 2.6$, and δ_I is approximately 180 \AA . In general, δ_I is in the order of several hundred angstroms. The expression of (17) is reminiscent of the similar expression for the penetration depth at radio frequencies

$$\delta = \frac{c}{\sqrt{4\pi\sigma_{d.c.}} \omega} = \frac{\lambda}{2\sqrt{2\pi} k} \quad \text{III-(18)}$$

where $\sigma_{d.c.}$ is the d.c. electric conductivity. The two expressions are essentially the same as far as the qualitative estimations are concerned.

Table II

Low Temperature Absorptivity of Metals

Metals	Total Absorptivity A		Bulk Absorptivity (A_B/A) %	Optical Data Used to Calculate A_B, A_s
	Present Theory	Experiment		
Cu	0.0048	0.0050 Biondi(1956)	40%	Beattie Conn (1955) Bor et al (1939) Forsterling + Freederickz (1913)
Al	0.008	—	49%	Golovashkin et al (1960) Motulevich et al (1960)
Ag	0.0046	0.0044 Biondi(1956)	20%	Schulz (1951, 1954) Hodgson (1955) Forsterling + Freederickz (1913)
Hg	0.030 [†]	—	87%	Schulz (1957)
Ga	0.037 [†]	—	87%	Schulz (1957)
Zn	$A_B = *$ 0.003	—	$A_B =$ 0.003	Hodgson (1955)
Sn	$A_B = *$ 0.008	—	$A_B =$ 0.008	Hodgson (1955)
Ni	0.015	—	86%	Beattie Conn (1955)
Tl	$A_B = *$ 0.054	—	$A_B =$ 0.054	Hass Bradford (1957)
Pt	0.054	—	94%	Forsterling Freederick (1913)
Ir	0.093	—	95%	Forsterling Freederick (1913)

[†] These are the extrapolations from the liquid data, and are not strictly valid for solids, except, perhaps, in the order of magnitude.

* The skin absorptivity A_s not computed.

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Chapter IV

Quantum Mechanical Calculation of Optical and Infrared Dispersion in Metals

IV-A Introduction

All of the existing theories are based on the common assumption that Maxwell's theory of electromagnetism is valid in the form that was discussed in Chapter II, and any new theory which is based on the same assumption should necessarily be formulated on the basic grounds laid by the work that has been done in the past.

The classical dispersion equations are simply the solutions to the equations of motion subject to Maxwell's electromagnetic field. Therefore, as long as we confine ourselves to that part of the spectrum where the free electrons are mostly responsible for the dispersion, it is quite natural for us to expect that a new theory which is offered by quantum mechanical calculations should necessarily be a "quantum mechanical free electron theory" which can differ from the classical free electron theory only in specification of the temperature dependence and also of further frequency dependence if any, in the viscous damping and polarizability, etc.

Various quantum mechanical dispersion equations should approach the corresponding classical equations in the limit

of low frequency where $\sigma(\omega)$ approaches the value of $\sigma(0)$ of the static case. It is hardly necessary to mention that some of the high frequency effects such as the phenomenon of anomalous dispersion arising from the photoelectric resonance of bound electrons and also of the small but important contribution of the core polarization can be explained rigorously only with the aid of quantum mechanics.

Further we already witnessed in Chapter III one consequence of quantum mechanical considerations at low temperature, namely the contribution of the anomalous skin effect to the absorptivity giving rise to a finite non-zero absorption at $0K^{\circ}$.

Compared with an enormous amount of qualitative and quantitative applications of quantum mechanics to the properties of metals under the influence of static electric fields, very little progress is found on the optical and infrared dispersive properties of metals beyond what is available from the classical free electron theories and the anomalous skin effects. The less said the better on similar considerations of alloys. However, it is self-evident that the noble features of quantum mechanics revealed in the metallic properties under the influence of static electric field provide an indispensable tool for examining the optical and infrared dispersion properties of metals, because as we saw in Chapter III, the two

aspects of metallic properties are intimately linked with each other. This was already qualitatively made use of in the early studies of Mott (1934) and Mott and Jones (1936). Further, much progress that has been made on the optical properties of semiconductors can be extended to metallic conductors with suitable modifications since, after all, the semiconductors and metallic conductors may be considered as differing from each other more in degree than in kind as far as the respective conduction mechanism and properties are concerned. The qualitative aspects of this feature was already discussed in the early studies of Wilson (1936) and more recently in the work of Bardeen and Shockley (1950).

Some of the considerations that enter in the quantum mechanical calculations may be mentioned as a) the Pauli exclusion principle; b) the Fermi-Dirac statistics; c) solid band structure; d) quantum mechanical interpretations of various interactions that contribute to the viscous damping of conduction electrons; e) the effect of core polarization; and f) the effect of the bound electrons. The calculations in the frame of the free electron theory involves considering explicitly all of the above except for the last two, in addition to the fundamental relations available from Maxwell's theory of electromagnetism considered in Chapter II. A qualitative discussion on the effects related with e) and f) was given in Chapter III, and excellent discussions of these

features, as to the mechanism and effects, are presented by Van Vleck (1959) and Mott and Jones (1936) on e) and f), respectively. A detailed discussion on these points is outside the scope of the present work.

In the theoretical calculations that will follow, it is attempted to find explicitly the ω - and T - dependent structure of the damping coefficient and hence the polarizability $\bar{\alpha}$ and also the bulk absorptivity $A_v(\omega, T)$, in the framework of the free electron theory and with the assumption of spherical Fermi surface. That very little error is involved in assuming a spherical energy surface for most of the body-centered, face-centered and hexagonal cubic lattices was pointed out by Wilson (1936) and Mott and Jones (1936), and is shown in the following qualitative expression for d.c. conductivity (Jones, 1956);

$$\sigma_{d.c.}^{ij} = + \frac{n_e e^2}{4\pi^3 \hbar^2} \iiint \left(- \frac{\partial F(E)}{\partial E} \right) \tau(\underline{k}) \left(\frac{\partial^2 E}{\partial k_i \partial k_j} \right) (d^3 \underline{k})$$

$$(i, j = 1, 2, 3)$$

where $F(E)$ is the dimensionless electron distribution function at energy $E(\underline{k})$ and $\tau(\underline{k})$ is the d.c. relaxation lifetime of an electron with momentum $(\hbar \underline{k})$. Furthermore, even for a metal which, in a single crystal, has a detectable degree of anisotropy, the spherical approximation of

Table IV
Metals with Large Anisotropy

Metals	<u>Anisotropy in d.c. resistivity</u>			Reference
	Max.	Min.	Ratio	
G_a (Solid)	55.(5)	7.8(5)	7	Powell (1949)
H_g (Solid)	23.5	17.8	1.32	Sckell (1930)
S_b	42.6	35.6	1.2	Bridgman (1925)
C_d	8.3	6.8	1.22	"
T_e	1.54×10^5	5.6×10^4	2.75	"
Z_n	6.05	5.83	1.04	"
B_i	138	109	1.27	"

Powell, Nature 164, 153 (1949)

Sckell, Ann. Physik (5) 6, 932 (1930)

Bridgman, Proc. Amer. Acad. 60, 306 (1925)

Fermi surface works well for a polycrystalline sample. Some particular cases of metals in which interband transitions make predominant contributions to various electrical and optical properties and for which nonspherical Fermi surface must be used, will be treated in the future chapter on transition metals.

The results on transition metals should apply equally well to other nontransition, multivalent metals when interband transitions need to be considered.

For metals to which spherical Fermi surface applies, effect of the periodic lattice is incorporated entirely into the effective number of electrons per unit volume and the effective mass. This is in accord with the "effective mass method" which will be discussed in more detail in the following section of this chapter. Then, for a metal which is free of impurities, the only perturbation to the electronic motion originating from the presence of lattice is the electron-phonon interaction or the interaction between the "free" electrons and the thermal vibrations of the lattice represented by a finite temperature-dependent distortion of the lattice from the perfectly periodic potential of 0°K. Such a perturbation decreases rapidly as temperature is lowered to the absolute zero. The metals with a substantial impurity content and alloys, especially the ones with a random lattice, are exceptions to this picture:

there is a finite, temperature-independent perturbation giving rise to a non-zero resistivity at 0°K, the total resistivity being given by this plus an additional temperature-dependent term (Mathiessen's rule), (Mathiessen and Vogt, 1864).

The bulk absorptivity A_v , the conductivity $\sigma(\omega)$ as well as the damping coefficient are calculated from the result on the rate of energy expenditure $\bar{W}(\omega, T)$, which is related to $\sigma(\omega)$, according to the free electron theory, by

$$n_e \bar{W} = \frac{E^2}{2} \sigma(\omega) \quad \text{IV-(1)}$$

where $\sigma(\omega)$ is in turn related to the damping coefficient through the typical free electron dispersion equations, and where $(E^2/2)$ is the energy density per unit volume of the electromagnetic radiation field.

Identification of the damping coefficient in the final expression of \bar{W} is straightforward when we compare the result with the corresponding d.c. expression derived in Wilson's theory of metals (1936). Thus, the approach adopted in the present work differs from the usual method of finding the damping coefficient directly by calculating the inverse of transition lifetimes (relaxation time) from the transition matrix elements.

IV-B Calculational Method and Assumptions on Damping Interactions

It will be assumed that the predominant contribution to the electron damping comes from the electron-lattice interaction in cooperation with the perturbing electromagnetic field. The contribution by electron-electron collisions, which are important at very high frequencies and at very low temperatures, will be combined with the results of the present chapter using the formulae obtained by Gurzhy (1958). Further, when metal contains a substantial amount of impurities, the effective damping will be the sum of the contributions by electron-phonon processes, electron-electron collisions and impurity scattering. The additional contribution by impurity scattering is responsible for the temperature-independent residual resistance in the Mathiessen rule. In the present chapter, calculations will be carried out for a pure metal. However, if the impurity effects need to be considered, a constant term is to be added to the damping coefficient. This additive constant may be calculated from either an optical data (Golovashkin et al, 1960) or from low temperature measurements of d.c. resistivity.

In this chapter, only those transitions which take place within a single band in the lowest Brillouin zone will

be considered: i.e., intraband transitions. The case where the interband transitions are involved will be left to a future chapter on transition metals.

Once we adopt the Hamiltonian in a specific form, various transition probabilities can be found by the usual quantum mechanical methods. We shall use the perturbation method similar to what was used by Wilson (1936) and Holstein (1954). Then, the transitions which are responsible for the damping and dispersion are the second-order processes in which an electron initially at the momentum state \underline{k}_1 makes a transition to the final state \underline{k}_2 upon simultaneous absorptions or emissions of a phonon and a photon.

We define

$$P_{(\pm)}^{(\pm)}(\underline{k}_1 \rightarrow \underline{k}_2)$$

as the probability per unit time for a conduction electron to make a transition from the state \underline{k}_1 to the final state \underline{k}_2 with simultaneous photon and phonon emissions (+) and absorptions (-) when it is certain that the \underline{k}_2 state is completely empty and \underline{k}_1 state is completely filled and where the superscript (\pm) designates the phonon processes and the subscript (\pm) the photon processes.

According to the Fermi-Dirac statistics, the probability that the state \underline{k} with the corresponding energy $E(\underline{k})$ is

filled at temperature $T(^{\circ}\text{K})$ is given by the Fermi function

$$f(E) = \frac{1}{1 + e^{\beta(E-E_F)}} \quad \text{IV-(2)}$$

where E_F is the Fermi energy and β is $(KT)^{-1}$, K being the Boltzmann constant. Then, the total probability per unit time of an electron initially at the state \underline{k}_1 to make a transition to any of the other empty states by either one of the four processes designated by the supercript and subscript (\pm) will be given by

$$P_{(\pm)}^{(\pm)}(\underline{k}_1) = 2 \sum_{\underline{k}_2} [1 - f(E_2)] P_{(\pm)}^{(\pm)}(\underline{k}_1 \rightarrow \underline{k}_2) \quad \text{IV-(3)}$$

where the factor 2 comes about because, according to the Pauli exclusion principle, two electrons with opposite spins can occupy the state with same \underline{k} and $E(\underline{k})$. The appearance of $[1-f(E_2)]$ embodies the Pauli exclusion principle.

In order to represent the gross manifestations of such microscopic transition processes, we have to average the probability of (3) over all the initially occupied states according to the Fermi-Dirac statistics. The resulting average value of probability $\langle P \rangle$ per unit time will be in the form

$$\langle P_{(s)}^{(r)} \rangle = 2 \sum_{\underline{k}_1} \sum_{\underline{k}_2} f(E_1) [1-f(E_2)] P_{(s)}^{(r)}(\underline{k}_1 \rightarrow \underline{k}_2) / \left(\sum_{\underline{k}_1} f(E_1) \right) \quad \text{IV-(4)}$$

where $r, s = (\pm)$.

Then, following Holstein (1954), the power expended by the electromagnetic radiation field is defined as

$$\bar{W} = \sum_{r=(\pm)} \hbar \omega \left[\langle P_{(-)}^{(r)} \rangle - \langle P_{(+)}^{(r)} \rangle \right] \quad \text{IV-(5)}$$

This implies simply that the net power expenditure is the total power absorbed minus the amount which is emitted into the radiation field. There is an analogy between (5) and the corresponding statistical mechanical formula of Wilson (1936).

The relation (5) is dependent on both the frequency ω and temperature T . A part of the temperature dependence comes from the Fermi-Dirac statistics of the electron distribution and the other part comes from the Bose-Einstein statistics of the phonon distribution (the thermal vibration of lattice) which enter in the Hamiltonian averaged over the distribution of phonon states.

Once the T - and ω -dependent expression for \bar{W} is obtained various dispersion formulae follow naturally. For instance, the high frequency conductivity $\sigma(\omega)$ is given by

$$n_e \bar{W} = \frac{E^2}{2} \sigma(\omega) \quad \text{IV-(6)}$$

Thus, it is evident that the main task of theoretical calculations is in finding correct values of \bar{W} or $\langle P \rangle$.

In general, the expression for \bar{W} will vary depending on the particular physical model of the system, the methods of computation, and the particular Hamiltonian that are adopted. According to the effective mass method of Peckar (1946), Slater (1949), Wannier (1937), and James (1949), and to the theorems developed by Bardeen and Shockley (1950), the electrons in an isotropic (cubic) lattice may be considered as free electrons of effective mass m^* , and when the lattice is distorted by a small amount resulting in a small change in the potential,

$$V_p = \delta U = U_d(\underline{x}) - U_o(\underline{x}) \quad \text{IV-(7)}$$

the amplitude part of the electronic wavefunction $A(\underline{x})$ satisfies the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m^*} \nabla^2 + \delta U \right] A(\underline{x}) = EA(\underline{x}) \quad \text{IV-(8)}$$

where $U_o(\underline{x})$ is the original undistorted periodic potential and $U_d(\underline{x})$ is the distorted potential which depends on the strains ϵ_{ij} that are imparted to the lattice in distortion. If the lattice is not cubic, we must replace $\left(\frac{1}{m^*} \nabla^2\right)$ by

$$\left(\frac{1}{m_1^*} \frac{\partial^2}{\partial x_1^2} + \frac{1}{m_2^*} \frac{\partial^2}{\partial x_2^2} + \frac{1}{m_3^*} \frac{\partial^2}{\partial x_3^2} \right)$$

where (x_1, x_2, x_3) are the three principal-axis coordinates, and (m_1^*, m_2^*, m_3^*) are the three values of effective mass. The amplitude function $A(\underline{x})$ is a smoothly varying function which does not vary appreciably over the unit cell: if $A(\underline{x})$ does not meet this condition, the method of effective mass is inadequate without a considerable degree of refinement. In general, wavefunctions of electrons in metals are rather flat except in the middle of the atom (Mott and Jones, 1936), and the volume within which the wavefunction is not flat is relatively small, so that the charge density in the flat region is almost exactly $\left(\frac{e}{V_0}\right)$, where V_0 is the atomic volume. This flatness of wavefunction is the reason why the approximation of neglecting the periodic field (free electron approximation) gives good results for metals, and thus Equation (8), should work. According to Bardeen and Shockley (1950), the electron-lattice potential $V_p(\underline{x})$ may be taken in the form

$$V_p(\underline{x}) = g \Delta(\underline{x}) \quad \text{IV-(9)}$$

where g is a constant and $\Delta(\underline{x})$ is the dilation. Neglecting the other terms in the expansion of $V_p(\underline{x})$ in powers of the strain ϵ_{ij} is equivalent to neglecting the dependence of the effective mass on the strain. It was shown that the

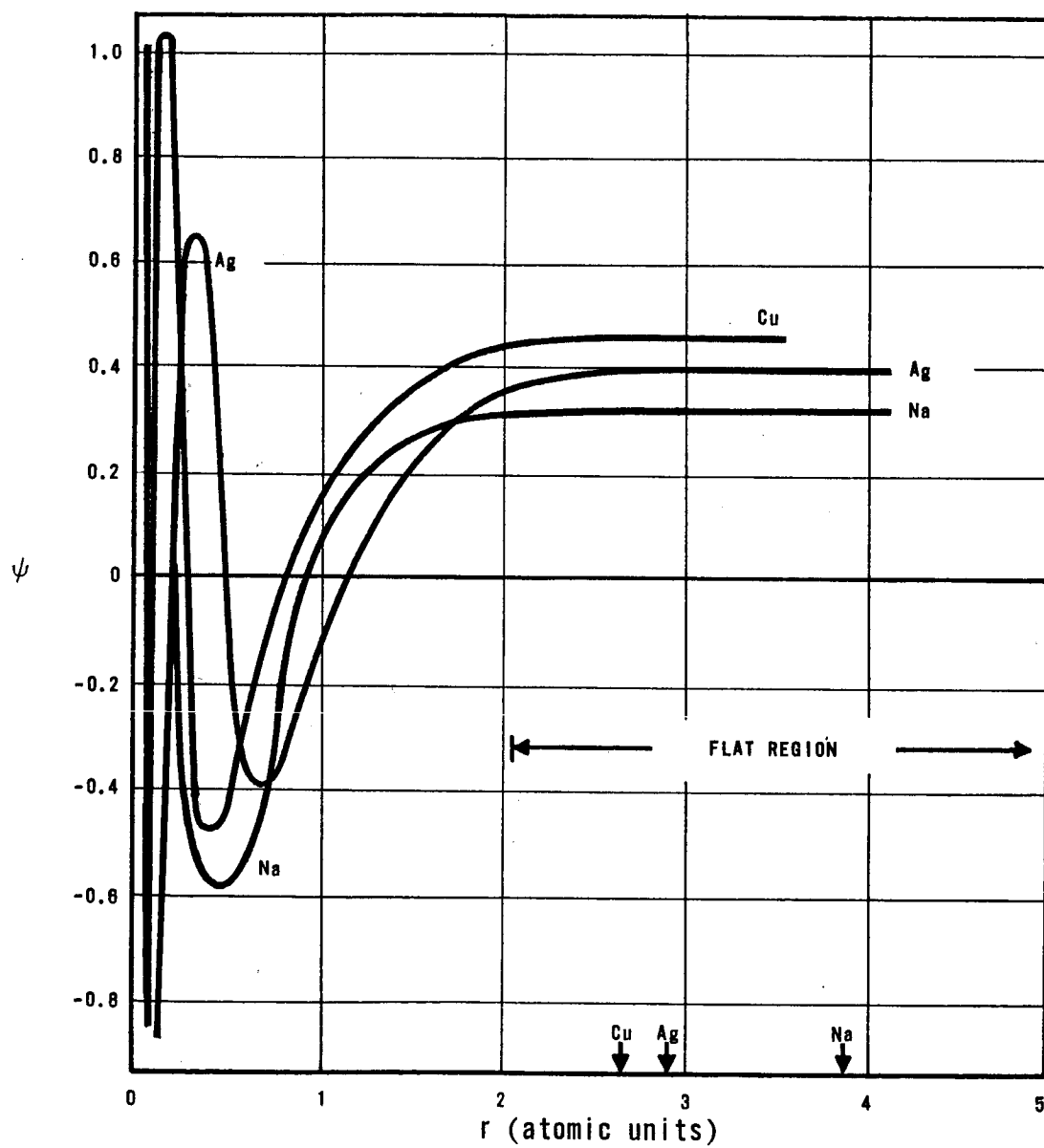


FIGURE 1

Electronic Wavefunctions of Metals

next largest term in $V_p(\underline{x})$ to that given in Equation (9) is proportional to the square of momentum times the strain

$$\sim 0(k^2 \times \text{strain})$$

and, for the usual order of magnitude of k^2 involved in metals and for the size of the strain in the thermal agitation of the lattice, this second term can safely be neglected.

IV-C Transition Probability Calculation

Following Bardeen and Shockley (1950) and Holstein (1954), the Schrödinger equation for a conduction electron interacting with the perturbing electromagnetic field \underline{A} and the lattice vibration may be written in the form

$$i\hbar \frac{\partial \psi}{\partial t} = \frac{1}{2m^*} \left(-i\hbar \nabla + \frac{e}{c} \underline{A} \right)^2 \psi + V_p(\underline{x}) \psi \quad \text{IV-(10)}$$

where $V_p(\underline{x})$ is interpreted as the electron-phonon interaction potential given by

$$V_p(\underline{r}) = g \operatorname{div} \underline{u}(\underline{r})$$

$$\underline{u}(\underline{r}) = \sum_{\underline{q}, j} \hat{e}_{\underline{q}, j} \left\{ a_j(\underline{q}) e^{i[\underline{q} \cdot \underline{r} - \omega_{\underline{q}, j} t]} + \text{c.c.} \right\} \quad \text{IV-(11)}$$

$$a_j(\underline{q}) = \sqrt{(\hbar N_{\underline{q}, j} / 2\rho_0 V \omega_{\underline{q}, j})}$$

$$a_j^*(\underline{q}) = \sqrt{(\hbar [N_{\underline{q}, j} + 1] / 2\rho_0 V \omega_{\underline{q}, j})}$$

where $(a_j^*(\underline{q}), a_j(\underline{q}))$ are the phonon creation and annihilation operators, ρ_0 is the mass density, $\omega_{\underline{q},j}$ is the phonon frequency

$$\hbar\omega_{\underline{q},j} = E_{\underline{q},j}$$

and $(\hat{e}_{\underline{q},j})$ are the orthonormal basic vectors,

$$(\hat{e}_{\underline{q},j} \cdot \hat{e}_{\underline{q},j}) = \delta_{jj},$$

and g is a constant whose value is of the same order as the electronic energy.

For an isotropic lattice, we have the simpler expression

$$V_p(\underline{x}) = ig \sum_{\underline{q}} q \left(\frac{\hbar^2}{2N_p M V E_{\underline{q}}} \right)^{\frac{1}{2}} \left[\sqrt{N(\underline{q})} e^{i(\underline{q} \cdot \underline{x} - E_{\underline{q}} t / \hbar)} \right.$$

IV-(12)

$$\left. - \sqrt{N(\underline{q}) + 1} e^{-i(\underline{q} \cdot \underline{x} - E_{\underline{q}} t / \hbar)} \right]$$

where we have used the following notations:

- M : Mass of the lattice
 V : The sample volume
 N_p : Phonon number density (per unit volume) = $\frac{\rho_0}{M}$
 \underline{q} : Phonon wave-vector (momentum/ \hbar)
 $E_{\underline{q}}$: Energy of a phonon at the state (\underline{q})
 $N(\underline{q})$: The number of phonon states for $E_{\underline{q}}$ that are occupied, and is according to Bose-Einstein statistics,

$$N(\underline{q}) = \frac{1}{e^{\beta E_{\underline{q}}} - 1}$$

In practice, it is often possible to distinguish longitudinal and transverse waves in a crystal and discard the latter because of the factor $(\hat{e}_j \cdot \underline{q})$ in Equation (11). This is what has been done in obtaining Equation (12). This is also related to the approximation of taking $E_{\underline{q}}$ dependent only on the magnitude q and using the simple Debye dispersion of phonons when the acoustic branch of phonon spectrum makes predominant contributions. When KT has a value comparable to the discrete quantum of upper branches, the optical branch contributes significantly.

In the present work, the electromagnetic field will be treated purely classically and we will use

$$\begin{aligned}\underline{A}(\underline{x}) &= \left(\underline{A}(\underline{x}) e^{-i\omega t} + \underline{A}^*(\underline{x}) e^{+i\omega t} \right) \\ &= -i \frac{e\underline{E}}{2\omega} \left(e^{i(\underline{p} \cdot \underline{x} - \omega t)} - e^{-i(\underline{p} \cdot \underline{x} - \omega t)} \right)\end{aligned}\quad \text{IV-(13)}$$

where \underline{E} is the electric amplitude vector which satisfies $(\underline{E} \cdot \underline{p}) = 0$ when we choose \underline{A} to meet the divergence condition $(\nabla \cdot \underline{A}) = 0$. The Schrödinger Equation (10) now becomes, upon neglecting the term quadratic in \underline{A} ,

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m^*} \nabla^2 \psi + \left(\frac{e\hbar}{im^*c} \underline{A} \cdot \nabla + V_p \right) \psi \quad \text{IV-(14)}$$

In the absence of the perturbation by the electromagnetic field and the lattice vibration, the stationary states of electrons are represented by the wavefunctions,

$$\psi_{\underline{k}}(\underline{x}, t) = e^{i(\underline{k} \cdot \underline{x} - E_{\underline{k}} t / \hbar)} \quad \text{IV-(15)}$$

where

$$E_{\underline{k}} = (\hbar^2 k^2 / 2m^*) \quad \text{IV-(16)}$$

The perturbed wavefunction $\psi(\underline{x}, t)$ may be expanded into a superposition of the unperturbed, free electron states in the form,

$$\psi(\underline{x}, t) = \sum_{\underline{k}} B(\underline{k}) \psi_{\underline{k}}(\underline{x}, t) \quad \text{IV-(17)}$$

where $B(\underline{k})$ is the expansion coefficient with an explicit time dependence. By substituting Equation (17) into (14), the equation of motion for $B(\underline{k})$ is obtained as

$$\begin{aligned}
 i\hbar \frac{\partial B(\underline{k})}{\partial t} = & \frac{e\hbar(\underline{k}, \underline{E})}{2im^*\omega} \left[B(\underline{k}-\underline{p}) e^{i(E_{\underline{k}} - E_{\underline{k}-\underline{p}} - \hbar\omega)t/\hbar} \right. \\
 & \left. - B(\underline{k}+\underline{p}) e^{i(E_{\underline{k}} - E_{\underline{k}+\underline{p}} + \hbar\omega)t/\hbar} \right] \\
 & + ig \sum_{\underline{q}} \left\{ q \left(\frac{\hbar^2}{2N_p MVE_{\underline{q}}} \right)^{\frac{1}{2}} \left[B(\underline{k}-\underline{q}) \sqrt{N(\underline{q})} e^{i(E_{\underline{k}} - E_{\underline{k}-\underline{q}} - E_{\underline{q}})t/\hbar} \right. \right. \\
 & \left. \left. - B(\underline{k}+\underline{q}) \sqrt{N(\underline{q})+1} e^{i(E_{\underline{k}} - E_{\underline{k}+\underline{q}} + E_{\underline{q}})t/\hbar} \right] \right\}
 \end{aligned}
 \tag{IV-18}$$

In the absence of the lattice vibration we would have only the first term [---] in Equation (18) arising solely from the electromagnetic field. In this case, the coefficient $B(\underline{k})$ cannot be made to increase indefinitely with time because the energy terms

$$E_{\underline{k}} - E_{\underline{k} \pm \underline{p}} \pm \hbar\omega$$

in the exponents cannot be made to vanish. In the language of perturbation theory, the transitions are at most virtual and this corresponds to the fact that a photon cannot be absorbed or emitted by a free electron. Therefore, the electromagnetic perturbation alone cannot explain the damping in optical dispersion (Heitler, 1957).

Following the usual procedure of the perturbation method, we write

$$B(\underline{k}) = \delta(\underline{k}, \underline{k}_0) + B_{(1)}(\underline{k}) + B_{(2)}(\underline{k}) + \dots \quad \text{IV-(19)}$$

where $B_{(1)}$, $B_{(2)} \dots$ are the first order, second order, ... terms for an electron which was certain to be at the state \underline{k}_0 initially. The electromagnetic and the lattice vibration terms will be considered as the first order perturbations in Equation (14). Then, $B_{(1)}$ in Equation (19) will contain only those terms which are in the first power of \underline{E} and g as well as those quadratic in each of \underline{E} and g . The combined action of the electromagnetic field and the lattice vibration is described by that term of $B_{(2)}$ which is bilinear in \underline{E} and g , and we will need only this part of $B_{(2)}$ for our dispersion calculations.

In order to calculate $B_{(2)}$, we need to obtain $B_{(1)}$ first. By substituting Equation (19) into (18) and collecting the terms which are of the first order in \underline{E} and g , and integrating in time from 0 to t , we obtain the following:

$$\begin{aligned}
 B_{(1)}(\underline{k}) &= \frac{ie\hbar(\underline{k}, \underline{E})}{2m^*\omega} \left[\delta(\underline{k}_0, \underline{k}-\underline{p}) \left(\frac{e^{i(\underline{E}_{\underline{k}} - \underline{E}_{\underline{k}-\underline{p}} - \hbar\omega)t/\hbar} - 1}{\underline{E}_{\underline{k}} - \underline{E}_{\underline{k}-\underline{p}} - \hbar\omega} \right) \right. \\
 &\quad \left. - \delta(\underline{k}_0, \underline{k}+\underline{p}) \left(\frac{e^{i(\underline{E}_{\underline{k}} - \underline{E}_{\underline{k}+\underline{p}} + \hbar\omega)t/\hbar} - 1}{\underline{E}_{\underline{k}} - \underline{E}_{\underline{k}+\underline{p}} + \hbar\omega} \right) \right. \\
 &\quad \left. - ig \sum_{\underline{q}} \left\{ q \left(\frac{\hbar^2}{2N_p M V E_{\underline{q}}} \right)^{\frac{1}{2}} \left[\delta(\underline{k}_0, \underline{k}-\underline{q}) \sqrt{N(\underline{q})} \left(\frac{e^{i(\underline{E}_{\underline{k}} - \underline{E}_{\underline{k}-\underline{q}} - E_{\underline{q}})t/\hbar} - 1}{\underline{E}_{\underline{k}} - \underline{E}_{\underline{k}-\underline{q}} - E_{\underline{q}}} \right) \right. \right. \right. \\
 &\quad \left. \left. - \delta(\underline{k}_0, \underline{k}+\underline{q}) \sqrt{N(\underline{q})+1} \left(\frac{e^{i(\underline{E}_{\underline{k}} - \underline{E}_{\underline{k}+\underline{q}} + E_{\underline{q}})t/\hbar} - 1}{\underline{E}_{\underline{k}} - \underline{E}_{\underline{k}+\underline{q}} + E_{\underline{q}}} \right) \right] \right\} \right]
 \end{aligned}
 \tag{IV-20}$$

Using Equation (20) in (18), and collecting only those terms which are bilinear in \underline{E} and \underline{g} , we obtain

$$\begin{aligned}
 B_{(2)}(\underline{k} \pm \underline{q} \pm \underline{p}) &= \left(\frac{\hbar^2 q^2}{2N_p M V E_{\underline{q}}} \right)^{\frac{1}{2}} \left(\frac{e\hbar g}{2m^*\omega} \right) \left\{ \frac{N(\underline{q})^{\frac{1}{2}}}{[N(\underline{q})+1]^{\frac{1}{2}}} \right\} \\
 \underline{E} \cdot &\left[\left(\frac{\underline{k} \pm \underline{q}}{\underline{E}_{\underline{k} \pm \underline{q}} - \underline{E}_{\underline{k}} \mp E_{\underline{q}}} + \frac{\underline{k}}{\underline{E}_{\underline{k} \pm \underline{p}} - \underline{E}_{\underline{k}} \mp \hbar\omega} \right) \frac{e^{i\xi t/\hbar} - 1}{\xi} \right. \\
 &\quad \left. - \frac{(\underline{k} \pm \underline{q})}{(\underline{E}_{\underline{k} \pm \underline{q}} - \underline{E}_{\underline{k}} \mp E_{\underline{q}})} \times \frac{e^{i\xi' t/\hbar} - 1}{\xi'} - \frac{\underline{k}}{(\underline{E}_{\underline{k} \pm \underline{p}} - \underline{E}_{\underline{k}} \mp \hbar\omega)} \frac{e^{i\xi'' t/\hbar} - 1}{\xi''} \right]
 \end{aligned}
 \tag{IV-21}$$

where \underline{k} is now written in place of \underline{k}_0 , and

$$\begin{aligned}
 \xi &= E_{\underline{k}+\underline{q}} - E_{\underline{k}} + \hbar\omega + E_{\underline{q}} \\
 \xi' &= E_{\underline{k}+\underline{q}+\underline{p}} - E_{\underline{k}+\underline{q}} + \hbar\omega \\
 \xi'' &= E_{\underline{k}+\underline{q}+\underline{p}} - E_{\underline{k}+\underline{p}} + E_{\underline{q}}
 \end{aligned}
 \tag{IV-22}$$

The probability per unit time, $P(\underline{k} \rightarrow \underline{k}+\underline{q}+\underline{p})$ for the electron to make a transition from \underline{k} to $(\underline{k}+\underline{q}+\underline{p})$ under the combined action of the electromagnetic and acoustical fields is given by the absolute square of $B_{(2)}$ divided by time,

$$\begin{aligned}
 P(\underline{k} \rightarrow \underline{k}+\underline{q}+\underline{p}) &= \left| B_{(2)}(\underline{k}+\underline{q}+\underline{p}) \right|^2 / t \\
 &: t \rightarrow \infty
 \end{aligned}
 \tag{IV-23}$$

A significant contribution to Equation (23) comes from those situations where one of the energy denominators contained in Equation (21) becomes zero. Only in such cases does the transition probability per unit time approach a constant nonvanishing value for a large t . The zeros of the energy denominators may be grouped into two categories: those which involve a coincidence of initial and final energies inclusive of the photon energy $\hbar\omega$ and phonon energy $E_{\underline{q}}$, and those which arise from an energy coincidence of an intermediate state with either the initial or final state. The two terms of Equation (21)

which contain ξ' and ξ'' will not contribute to the over-all transition probability, since they cancel out in calculations of the energy expenditure. It is easily shown that

$$|\xi'| \approx \left| 1 + \frac{v_F}{c} \right| \hbar\omega \approx \hbar\omega$$

On the other hand, the zero, $\xi''=0$, is physically possible and the resonance factor containing ξ'' gives rise to $\delta(\xi'')$ in the expression for the transition probability. However, the terms with ξ' and ξ'' contribute equally to both absorption and emission processes of photons, and the over-all contribution from these terms to the net absorption, which is obtained from

$$\left(P_{(-)}^{(+)} - P_{(+)}^{(+)} \right)$$

cancel out. Therefore, we only need to evaluate the transition probability at the singularity $\xi=0$.

Equation (21) may then be replaced by equation,

$$B_{(2)}(\underline{k} \pm \underline{q} \pm \underline{p}) = q \left(\frac{\hbar^2}{2N_p M V E_q} \right)^{\frac{1}{2}} \left(\frac{\sqrt{N(q)}}{\sqrt{N(q)+1}} \right) \frac{e\hbar g}{2m^*\omega}$$

IV-(24)

$$\times \underline{E} \cdot \left(\frac{\underline{k} \pm \underline{q}}{E_{\underline{k} \pm \underline{q}} - E_{\underline{k}} \mp E_{\underline{q}}} + \frac{\underline{k}}{E_{\underline{k} \pm \underline{p}} - E_{\underline{k}} \mp \hbar\omega} \right) \frac{e^{i(E_{\underline{k} \pm \underline{q} \pm \underline{p}} - E_{\underline{k}} \mp E_{\underline{q}} \mp \hbar\omega)t/\hbar} - 1}{E_{\underline{k} \pm \underline{q} \pm \underline{p}} - E_{\underline{k}} \mp \hbar\omega \mp E_{\underline{q}}}$$

Let us consider the transitions $\underline{k} \rightarrow (\underline{k}+\underline{q}+\underline{p})$ first.

We notice that

$$\begin{aligned} & \left(E_{\underline{k}+\underline{q}} - E_{\underline{k}} - E_{\underline{q}} \right) + \left(E_{\underline{k}+\underline{p}} - E_{\underline{k}} - \hbar\omega \right) = \\ & \left(E_{\underline{k}+\underline{p}} - E_{\underline{k}} \right) - \left(E_{\underline{k}+\underline{q}+\underline{p}} - E_{\underline{k}+\underline{q}} \right) + \xi \cong 0 \end{aligned} \quad \text{IV-(25)}$$

The quantities of the form $\left(E_{\underline{k}+\underline{p}} - E_{\underline{k}} \right)$ represent the (v/c) corrections, and will be ignored. Furthermore, ξ may be taken equal to zero in Equation (25); a deviation from zero need be considered only in the last factor of Equation (24) representing the resonance factor.

Equation (24) is then replaced by

$$\begin{aligned} B_{(2)}(\underline{k}+\underline{q}+\underline{p}) &= q \left(\frac{\hbar^2}{2N_p MVE_q} \right)^{\frac{1}{2}} \sqrt{N(q)} \frac{e\hbar g}{2m^*\omega} \\ &\times \frac{E \cdot q}{\hbar\omega + E_{\underline{k}} - E_{\underline{k}+\underline{p}}} \times \frac{e^{i\xi t/\hbar} - 1}{\xi} \end{aligned} \quad \text{IV-(26)}$$

for the transition, $\underline{k} \rightarrow \underline{k}+\underline{q}+\underline{p}$.

The transition probability $P(\underline{k} \rightarrow \underline{k}+\underline{q}+\underline{p})$ may be evaluated readily from Equation (26) upon taking

$$\left(E_{\underline{k}+\underline{p}} - E_{\underline{k}} - \hbar\omega \right) \cong -\hbar\omega$$

and following the popular practice (Heitler, 1957),

$$\begin{aligned}\delta(\xi) &= \lim_{t \rightarrow \infty} \frac{\hbar}{2\pi} \frac{1}{t} \left| \frac{-i}{\hbar} \int_0^t e^{i\xi t'/\hbar} dt' \right|^2 \\ &= \lim_{t \rightarrow \infty} \frac{\hbar}{2\pi} \frac{1}{t} \left| \frac{e^{i\xi t/\hbar} - 1}{\xi} \right|^2\end{aligned}\quad \text{IV-(27)}$$

We thus have

$$P(\underline{k} \rightarrow \underline{k} + \underline{q} + \underline{p}) = \frac{\pi g^2 N(\underline{q}) e^2 \hbar^3 q^2}{4 N_p M V E_{\underline{q}} m^{*2} \omega^2} \frac{(\underline{E} \cdot \underline{q})^2}{(\hbar \omega)^2} \delta(\xi) \quad \text{IV-(28)}$$

Upon introducing the final state momentum \underline{k}_2 as $(\underline{k} + \underline{q} + \underline{p})$ and denoting the initial state \underline{k} as \underline{k}_1 , and noting also that the argument ξ of the delta function $\delta(\xi)$ represents the absorption of a phonon and a photon of energy $\hbar\omega$ and E_q respectively, we may rewrite (28) into the form

$$P_{(-)}^{(-)}(\underline{k}_1 \rightarrow \underline{k}_2) = \frac{\pi \hbar q^2 N(q) e^2 g^2}{4 N_p M V E_{\underline{q}} m^{*2} \omega^4} (\underline{E} \cdot \underline{q})^2 \delta(E_2 - E_1 - E_q - \hbar\omega) \quad \text{IV-(29)}$$

where the superscript $(-)$ refers to the phonon absorption and the subscript $(-)$ to the photon absorption.

From now on, the photon momentum \underline{p} will be neglected for the reason stated previously, and represent the final momentum \underline{k}_2 as

$$\underline{k}_2 = \underline{k}_1 + \underline{q} \quad \text{IV-(30)}$$

Then, Equation (29) may readily be generalized to include the emissions (+) of phonons and photons as well, and we have the general formula,

$$P_{(\pm)}^{(\pm)}(\underline{k}_1 \rightarrow \underline{k}) = \frac{e^2(\underline{E} \cdot \underline{q})^2}{4V_m \omega^4} G^{(\pm)}(\underline{q}) \delta(E_2 - E_1 \pm \hbar\omega) \quad \text{IV-(31)}$$

where

$$G^{(\pm)}(\underline{q}) = \frac{\pi \hbar q^2 g^2}{N_p M E_q} \begin{pmatrix} N(\underline{q}) + 1 \\ N(\underline{q}) \end{pmatrix} \quad \text{IV-(32)}$$

which are proportional to the probabilities of absorption (-) and emission (+) of phonons without scattering (Wilson, 1936; Born and Huang, 1956).

Next we evaluate $\langle P_{(s)}^{(r)} \rangle$ ($r, s = \pm$) from Relations (3) and (4). Substitution of Equation (31) into (3) gives us

$$P_{(s)}^{(r)}(\underline{k}_1) = \sum_{\underline{k}_2} \frac{e^2(\underline{E} \cdot \underline{q})^2}{2V_m \omega^4} G^{(r)}(\underline{q}) [1 - f(E_2)] \delta(E_2 - E_1 + r\hbar\omega) \quad \text{IV-(33)}$$

The summation over the final momentum states \underline{k}_2 may be replaced by corresponding momentum integral,

$$\begin{aligned}\delta(\xi) &= \lim_{t \rightarrow \infty} \frac{\hbar}{2\pi} \frac{1}{t} \left| \frac{-i}{\hbar} \int_0^t e^{i\xi t'/\hbar} dt' \right|^2 \\ &= \lim_{t \rightarrow \infty} \frac{\hbar}{2\pi} \frac{1}{t} \left| \frac{e^{i\xi t/\hbar} - 1}{\xi} \right|^2\end{aligned}\quad \text{IV-(27)}$$

We thus have

$$P(\underline{k} \rightarrow \underline{k} + \underline{q} + \underline{p}) = \frac{\pi g^2 N(\underline{q}) e^2 \hbar^3 \underline{q}^2}{4 N_p M V E_{\underline{q}} m^{*2} \omega^2} \frac{(\underline{E} \cdot \underline{q})^2}{(\hbar \omega)^2} \delta(\xi) \quad \text{IV-(28)}$$

Upon introducing the final state momentum \underline{k}_2 as $(\underline{k} + \underline{q} + \underline{p})$ and denoting the initial state \underline{k} as \underline{k}_1 , and noting also that the argument ξ of the delta function $\delta(\xi)$ represents the absorption of a phonon and a photon of energy $\hbar\omega$ and $E_{\underline{q}}$ respectively, we may rewrite (28) into the form

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where the superscript $(-)$ refers to the phonon absorption and the subscript $(-)$ to the photon absorption.

From now on, the photon momentum \underline{p} will be neglected for the reason stated previously, and represent the final momentum \underline{k}_2 as

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Then, Equation (29) may readily be generalized to include the emissions (+) of phonons and photons as well, and we have the general formula,

$$P_{(\pm)}^{(\pm)}(\underline{k}_1 \rightarrow \underline{k}) = \frac{e^2(\underline{E} \cdot \underline{q})^2}{4V m^* \omega^4} G^{(\pm)}(\underline{q}) \delta(E_2 - E_1 \pm \hbar\omega) \quad \text{IV-(31)}$$

where

$$G^{(\pm)}(\underline{q}) = \frac{\pi \hbar q^2 g^2}{N_p M E_q} \binom{N(\underline{q})+1}{N(\underline{q})} \quad \text{IV-(32)}$$

which are proportional to the probabilities of absorption (-) and emission (+) of phonons without scattering (Wilson, 1936; Born and Huang, 1956).

Next we evaluate $\langle P_{(s)}^{(r)} \rangle (r, s = \pm)$ from Relations (3) and (4). Substitution of Equation (31) into (3) gives us

$$P_{(s)}^{(r)}(\underline{k}_1) = \sum_{\underline{k}_2} \frac{e^2(\underline{E} \cdot \underline{q})^2}{2V m^* \omega^4} G^{(r)}(\underline{q}) [1 - f(E_2)] \delta(E_2 - E_1 + r\hbar\omega) \quad \text{IV-(33)}$$

The summation over the final momentum states \underline{k}_2 may be replaced by corresponding momentum integral,

$$\begin{aligned} \sum_{\underline{k}_2} &\rightarrow \frac{V}{(2\pi)^3} \iiint (d\underline{k}_2) \dots \\ d\underline{k}_2 &= k_2^2 dk_2 d\Omega_2 \\ &= \frac{dE_2}{|\text{grad } E_2|} dS_{\underline{k}_2} : dS_{\underline{k}_2} = k_2^2 d\Omega_2 \end{aligned} \quad \text{IV-(34)}$$

In virtue of the relation, $q = \pm(\underline{k}_2 - \underline{k}_1)$, the summation over \underline{k}_2 is equivalent to summation over the phonon momentum \underline{q} and also to replacing the summation by the corresponding integral in momentum space,

$$\sum_{\underline{q}} \rightarrow \frac{V}{(2\pi)^3} \iiint (d\underline{q}) \dots \quad \text{IV-(35)}$$

At the same time, it is expedient to average over the direction of the electric field with respect to \underline{q} .

One thus obtains

$$\begin{aligned} P_{(s)}^{(r)}(\underline{k}_1) &= \frac{c^2 E^2}{48\pi^3 m^{*2} \omega^4} \int_0^{r_0} q^4 dq \int_{-1}^{+1} d\mu G^{(r)}(\underline{q}) [1 - f(E_2)] \\ &\times \delta\left(\frac{\hbar^2 q^2}{2m^*} + \frac{\hbar^2}{m^*} k_1 q \mu + r E_q + s \hbar \omega\right) \end{aligned} \quad \text{IV-(36)}$$

where we have taken $\overline{(\underline{E} \cdot \underline{q})^2} = \frac{1}{3} q^2 E^2$ and $\mu = \cos \theta$, θ being the angle between the momenta, \underline{k}_1 and \underline{q} , and $E_2 = E_2(\underline{k}_1 \pm \underline{q})$.

The integral over q extends from 0 to the maximum value q_0 where q_0 is determined from the Debye temperature Θ and the longitudinal phase velocity of sound u_L by the relation,

$$\hbar u_L q_0 = K\Theta \quad \text{IV-(37)}$$

where K is the Boltzmann constant. It is also determined equivalently from the phonon number density N_p per unit volume,

$$N_p = \frac{4\pi}{3} \frac{1}{(2\pi)^3} q_0^3 = q_0^3 / 6\pi^2 \quad \text{IV-(38)}$$

Here we have assumed the simple Debye dispersion of phonons. This approximation is known to be satisfactory at ordinary temperatures, such as in heat capacity calculations. The shortcomings of the Debye model of lattice appear mostly at very high temperatures where the average momentum transfer in electronic processes is considerably larger than the Debye cut-off value, and also at very low temperatures. More complete formulation of phonon dispersion is available; see, for instance, Leighton (1948) on monovalent metals and Bardeen (1937) for a more rigorous form of electron-phonon interaction involving the Umklapp processes important at very high temperatures. The work of Leighton (1948) shows that a more general

treatment than Debye's model of the lattice dispersion leads to formulae which are essentially the same as those obtained from the Debye theory, except at very high temperatures. The difference is that the Debye temperature Θ is no more a constant but contains a small temperature-dependence. The deviation of Θ from the value determined from room temperature measurement of heat capacity, for instance, becomes more enhanced at lower temperatures. The temperature-dependence in Θ has also been discussed by Wilson (1936).

In general, the usual Debye temperature Θ and its low-temperature value Θ_0 (notation used by Wilson) are in the same order of magnitude. It is expected, therefore, that, as long as the Debye cut-off is used as a parameter which is to be adjusted within a small margin in the neighborhood of its room temperature value, the Debye theory is satisfactory in the present formulation. Furthermore, it will be shown that various optical and infrared dispersion properties are not very sensitive to a small variation in Θ .

The delta function in Equation (36) is eliminated by integrating over μ from (-1) to $(+1)$. The existence of a real μ such that the argument of the delta function vanishes for all q between zero and q_0 , has been asserted by Wilson (1936) in his calculations of d.c. conductivity. That the same can be asserted in the present work involving

an electromagnetic field is shown in the appendix.

$$P_{(s)}^{(r)}(\underline{k}_1) = \frac{e^2 E^2}{24\pi^2 m^* \omega^4 \hbar^2 k_1} \int_0^{q_0} q^3 dq G^{(r)}(q) [1 - f(E_1 - rE_q - s\hbar\omega)] \quad \text{IV-(39)}$$

In obtaining Equations (36) and (39), it has been assumed that $N(\underline{q})$, $E_{\underline{q}}$ and hence $G^{(r)}(q)$ depend only on the magnitude q and not on the angular variables. The only part of Equation (33) where the dependence on the azimuthal angle appears was in $(\underline{E} \cdot \underline{q})^2$ with \underline{k}_1 as the polar axis. The argument of $f(---)$ in Equation (39) results from satisfying the delta function after integration over μ . Calculation of $\langle P_{(s)}^{(r)} \rangle$ proceeds by multiplying (39) by the Fermi function $f(E_1)$ and summing it up over the initial momentum state \underline{k}_1 , and dividing the entire expression by the normalization,

$$\sum_{\underline{k}_1} f(E_1)$$

In these calculations, we shall assume that the Fermi energy E_f obeys the condition,

$$E_f \gg \hbar\omega, \quad KT \quad \text{IV-(40)}$$

Thus, it is equivalently assumed that, for the frequency range that is of interest, most of the transitions take place in the neighborhood of the Fermi level,

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$$E_f \gg \hbar\omega, \quad KT \quad \text{IV-(40)}$$

Thus, it is equivalently assumed that, for the frequency range that is of interest, most of the transitions take place in the neighborhood of the Fermi level,

and $P_{(s)}^{(r)}(\underline{k}_1)F(E_1)$ differs from zero only in the neighborhood of $E_1 \simeq E_f$. With these assumptions being considered, the density-of-states factor $\sqrt{E_1}$ may be taken out of the integral set equal to $\sqrt{E_f}$. Then, we obtain

$$\begin{aligned} \langle P_{(s)}^{(r)} \rangle &= \left(\sum_{\underline{k}_1} f(E_1) \right)^{-1} \times \sum_{\underline{k}_1} f(E_1) P_{(s)}^{(r)}(\underline{k}_1) \\ &\cong \frac{e^2 E^2}{16\pi^2 m^* \omega^4 \hbar^2 k_0 E_f} \int_0^{q_0} q^3 dq G^{(r)}(q) F_{(s)}^{(r)}(q) \end{aligned} \quad \text{IV-(41)}$$

where $F_{(s)}^{(r)}(q)$ is the integral,

$$\begin{aligned} F_{(s)}^{(r)}(q) &= \frac{1}{\beta} \int_{-\infty}^{+\infty} dz \frac{e^z}{1+e^z} \cdot \frac{1}{1+e^{z+a}} \\ z &= \beta(E_1 - E_f - rE_q - s\hbar\omega) \\ a &= \beta(rE_q + s\hbar\omega) \end{aligned} \quad \text{IV-(42)}$$

The integral $F_{(s)}^{(r)}(q)$ can be evaluated exactly, and we have

$$F_{(s)}^{(r)}(q) = (rE_q + s\hbar\omega) / \left[e^{\beta(rE_q + s\hbar\omega)} - 1 \right] \quad \text{IV-(43)}$$

The power expenditure $\bar{W}(\omega)$ which was defined in Equation (5), can be evaluated using Equations (41) and (43), and

$$\hbar u_L q = E_q = \hbar \omega_q \quad \text{IV-(44)}$$

along with the Relations (37) and (38), and it is in the form

$$\bar{W}(\omega) = \sum_{r=\pm} \frac{e^2 E^2}{16\pi^2 m^* \hbar \omega^3 k_0 E_f} \int_0^{q_0} q^3 dq G^{(r)} \left[F_{(-)}^{(r)} - F_{(+)}^{(r)} \right] \quad \text{IV-(45)}$$

We substitute $G^{(r)}$ of Equation (32) into (45) and use

$$N(q) = 1 / e^{\beta E_q} - 1$$

In order to obtain the power expenditure per unit volume, it is expedient to introduce the effective number of electrons per unit volume, n_e . After some algebraic manipulations, we finally obtain,

$$n_e \bar{W} = \frac{n_e e^2}{m^*} R \left(\frac{T}{\Theta} \right)^5 \frac{E^2}{2\omega^2} Z(\omega, T) \quad \text{IV-(46)}$$

where R is constant given by

$$R = \frac{9\pi^3}{2} \hbar^2 g^2 N_p / (2m^* E_f^3)^{\frac{1}{2}} MK\Theta \quad \text{IV-(47)}$$

and $Z(\omega, T)$ is a function of both ω and T given by

$$J(\mu, \alpha) = \frac{e^\mu \sinh(\mu)}{\mu} \left\{ J_5(\mu, \alpha) - \frac{(e^\mu - 1)^2}{e^{2\mu} - 1} \mu J_4(\mu, \alpha) \right. \\ \left. - 2 \frac{(e^\mu - 1)^2}{e^{2\mu} - 1} \mu K_4(\mu, \alpha) \right\} \quad \text{IV-(48)}$$

and $P_{(s)}^{(r)}(\underline{k}_1)F(E_1)$ differs from zero only in the neighborhood of $E_1 \simeq E_f$. With these assumptions being considered, the density-of-states factor $\sqrt{E_1}$ may be taken out of the integral set equal to $\sqrt{E_f}$. Then, we obtain

$$\begin{aligned} \langle P_{(s)}^{(r)} \rangle &= \left(\sum_{\underline{k}_1} f(E_1) \right)^{-1} \times \sum_{\underline{k}_1} f(E_1) P_{(s)}^{(r)}(\underline{k}_1) \\ &\cong \frac{e^2 E^2}{16\pi^2 m^* \omega^4 \hbar^2 k_0 E_f} \int_0^{q_0} q^3 dq G^{(r)}(q) F_{(s)}^{(r)}(q) \end{aligned} \quad \text{IV-(41)}$$

where $F_{(s)}^{(r)}(q)$ is the integral,

$$\begin{aligned} F_{(s)}^{(r)}(q) &= \frac{1}{\beta} \int_{-\infty}^{+\infty} dz \frac{e^z}{1+e^z} \cdot \frac{1}{1+e^{z+a}} \\ z &= \beta(E_1 - E_f - rE_q - s\hbar\omega) \\ a &= \beta(rE_q + s\hbar\omega) \end{aligned} \quad \text{IV-(42)}$$

The integral $F_{(s)}^{(r)}(q)$ can be evaluated exactly, and we have

$$F_{(s)}^{(r)}(q) = (rE_q + s\hbar\omega) / \left[e^{\beta(rE_q + s\hbar\omega)} - 1 \right] \quad \text{IV-(43)}$$

The power expenditure $\bar{W}(\omega)$ which was defined in Equation (5), can be evaluated using Equations (41) and (43), and

$$\hbar u_L q = E_q = \hbar \omega_q \quad \text{IV-(44)}$$

along with the Relations (37) and (38), and it is in the form

$$\bar{W}(\omega) = \sum_{r=\pm} \frac{e^2 E^2}{16\pi^2 m^* \hbar \omega^3 k_0 E_f} \int_0^{q_0} q^3 dq G^{(r)} \left[F_{(-)}^{(r)} - F_{(+)}^{(r)} \right] \quad \text{IV-(45)}$$

We substitute $G^{(r)}$ of Equation (32) into (45) and use

$$N(q) = 1 / e^{\beta E_q} - 1$$

In order to obtain the power expenditure per unit volume, it is expedient to introduce the effective number of electrons per unit volume, n_e . After some algebraic manipulations, we finally obtain,

$$n_e \bar{W} = \frac{n_e e^2}{m^*} R \left(\frac{T}{\Theta} \right)^5 \frac{E^2}{2\omega^2} Z(\omega, T) \quad \text{IV-(46)}$$

where R is constant given by

$$R = \frac{9\pi^3}{2} \hbar^2 g^2 N_p / (2m^* E_f^3)^{\frac{1}{2}} MK\Theta \quad \text{IV-(47)}$$

and $Z(\omega, T)$ is a function of both ω and T given by

$$J(\mu, \alpha) = \frac{e^\mu \sinh(\mu)}{\mu} \left\{ J_5(\mu, \alpha) - \frac{(e^\mu - 1)^2}{e^{2\mu} - 1} \mu J_4(\mu, \alpha) \right. \\ \left. - 2 \frac{(e^\mu - 1)^2}{e^{2\mu} - 1} \mu K_4(\mu, \alpha) \right\} \quad \text{IV-(48)}$$

where

$$\mu = \left(\frac{\hbar \omega}{KT} \right) ; \quad \alpha = \left(\frac{\Theta}{T} \right)$$

$$J_n(\mu, \alpha) = \int_0^\alpha y^n dy / (e^y - e^\mu) (e^\mu - e^{-y})$$

$$K_n(\mu, \alpha) = \int_0^\alpha y^n dy / (e^y - e^\mu) (e^\mu - e^{-y}) (e^y - 1)$$

IV-(49)

This is the basic relation from which important dispersion relations will be obtained in the succeeding parts of this chapter.

A close examination of relations (48) and (49) reveals that $Z(\mu, \alpha)$ approaches values which are independent of μ and hence ω in the limit of $\mu \gg \alpha$ and also when $\mu \rightarrow 0$. In particular, when $\mu \rightarrow 0$, we have

$$Z(\mu, \alpha) \sim J_5^0(\alpha)$$

IV-(50)

where

$$J_5^0(\alpha) = \int_0^\alpha y^5 dy / (e^y - 1) (1 - e^{-y}) = J_5(\mu, \alpha) \Big|_{\mu=0}$$

IV-(51)

This is identified with Wilson's $J_5\left(\frac{\Theta}{T}\right)$, and, more important, with Grüneisen's formula (Grüneisen, 1933) for temperature-dependence of d.c. resistivity when we multiply by α^{-5} .

The ω -dependent quantity $Z(\mu, \alpha)$ has no precedence in the classical theories and hence constitutes an important consequence of the present theory.

For the coming discussions on dispersion properties, it is convenient to define the quantity $b_{ep}(\mu, \alpha)$, the subscript e.p. signifying the electron-phonon processes, such that

$$b_{ep}(\mu, \alpha) = \frac{Z(\mu, \alpha)}{Z(0, \alpha)} = \frac{1}{J_5^0(\alpha)} Z(\mu, \alpha) \quad \text{IV-(52)}$$

The numerical values of $b_{ep}(\mu, \alpha)$ can be obtained when we evaluate the values of $J_n(\mu, \alpha)$ and $K_n(\mu, \alpha)$ for arbitrary values of ω and T . The d.c. quantities $J_n^0(\alpha)$ and $K_n^0(\alpha)$ have been discussed in many references and are available in calculable forms. All types of integrals which enter in evaluation of $b_{ep}(\mu, \alpha)$ are discussed in the appendix, and the results are given as follows; (for $n > 0$)

$$\begin{aligned} J_n(\mu, \alpha) = & \frac{1}{e^{2\mu}-1} \sum_{m=0}^n \frac{1}{m+1} \mu^{n-m} \binom{n}{m} \left[\left[\frac{(\alpha-\mu)^{m+1}}{e^{\alpha-\mu}-1} \right. \right. \\ & + (-1)^{n-m+1} \frac{(\alpha+\mu)^{m+1}}{e^{\alpha+\mu}-1} - (-1)^{m+1} (e^\mu + [-1]^n) \frac{\mu^{m+1}}{e^\mu-1} \\ & + J_{m+1}^0(\alpha-\mu) + (-1)^{n-m+1} J_{m+1}^0(\alpha+\mu) \\ & \left. \left. - (-1)^{m+2} J_{m+1}^0(\mu) (1 + [-1]^{n+1}) \right] \right] \end{aligned} \quad \text{IV-(53)}$$

$$\begin{aligned}
 K_n(\mu, \alpha) = & \frac{1}{(e^{2\mu}-1)(e^\mu-1)} \left[\sum_{m=0}^n \frac{1}{m+1} \mu^{n-m} \binom{n}{m} \left\{ e^\mu (-1)^{n-m} \left[\frac{(\mu+\alpha)^{m+1}}{e^{\mu+\alpha}-1} - \frac{\mu^{m+1}}{e^\mu-1} \right] \right. \right. \\
 & + e^\mu (-1)^{n-m} \left[J_{m+1}^0(\alpha+\mu) - J_{m+1}^0(\mu) \right] + \frac{(\alpha-\mu)^{m+1}}{e^{\alpha-\mu}-1} - (-1)^{m+1} \frac{\mu^{m+1}}{e^{-\mu}-1} \\
 & + \left[J_{m+1}^0(\alpha-\mu) + (-1)^{m+1} J_{m+1}^0(\mu) \right] - (m+1) e^\mu (-1)^{n-m} \zeta_m(\alpha+\mu; \mu) \\
 & - (m+1) \zeta_m(\alpha-\mu; -\mu) \left. \right\} - \frac{(1+e^\mu)}{n+1} \frac{\alpha^{n+1}}{e^\alpha-1} - \frac{(1+e^\mu)}{n+1} J_{n+1}^0(\alpha) \\
 & - (1+e^\mu) \zeta_m(\alpha; 0) \Bigg]
 \end{aligned} \tag{IV-54}$$

where $J_{m+1}^0(x)$ is the same as what was defined in equation (51) with the only difference that the upper limit α in equation (51) is to be replaced by x , and

$$\zeta_n(a; b) = \int_b^a y^n dy e^{-y} \tag{IV-55}$$

Numerical evaluation of the d.c. quantities $\{J_n^0(x)\}$ is considerably simplified in the limiting cases, $x \ll 1$ (high temperature) and $x \gg 1$ (low temperature).

For $x \ll 1$, we have

$$J_m^0(x) \cong \int_0^x (y^{n-2} - \frac{7}{12} y^n + \dots) dy = \frac{1}{n-1} x^{n-1} - \frac{7}{12(n+1)} x^{n+1} + \dots \quad \text{IV-(56)}$$

and for $x \gg 1$,

$$J_n^0(x) \cong J_n^0(\infty) = n \int_0^\infty \frac{y^{n-1} dy}{e^y - 1} = n! \sum_{r=1}^\infty \frac{1}{r^n} \quad \text{IV-(57)}$$

(e.g. $J(\infty) = 124.4$)

$$\begin{aligned}
 K_n(\mu, \alpha) = & \frac{1}{(e^{2\mu}-1)(e^\mu-1)} \left[\sum_{m=0}^n \frac{1}{m+1} \mu^{n-m} \binom{n}{m} \left\{ e^\mu (-1)^{n-m} \left[\frac{(\mu+\alpha)^{m+1}}{e^{\mu+\alpha}-1} - \frac{\mu^{m+1}}{e^\mu-1} \right] \right. \right. \\
 & + e^\mu (-1)^{n-m} \left[J_{m+1}^0(\alpha+\mu) - J_{m+1}^0(\mu) \right] + \frac{(\alpha-\mu)^{m+1}}{e^{\alpha-\mu}-1} - (-1)^{m+1} \frac{\mu^{m+1}}{e^{-\mu}-1} \\
 & + \left[J_{m+1}^0(\alpha-\mu) + (-1)^{m+1} J_{m+1}^0(\mu) \right] - (m+1) e^\mu (-1)^{n-m} \zeta_m(\alpha+\mu; \mu) \\
 & - (m+1) \zeta_m(\alpha-\mu; -\mu) \left. \right\} - \frac{(1+e^\mu)}{n+1} \frac{\alpha^{n+1}}{e^\alpha-1} - \frac{(1+e^\mu)}{n+1} J_{n+1}^0(\alpha) \\
 & - (1+e^\mu) \zeta_m(\alpha; 0) \Bigg]
 \end{aligned} \tag{IV-54}$$

where $J_{m+1}^0(x)$ is the same as what was defined in equation (51) with the only difference that the upper limit α in equation (51) is to be replaced by x , and

$$\zeta_n(a; b) = \int_b^a y^n dy e^{-y} \tag{IV-55}$$

Numerical evaluation of the d.c. quantities $\{J_n^0(x)\}$ is considerably simplified in the limiting cases, $x \ll 1$ (high temperature) and $x \gg 1$ (low temperature).

For $x \ll 1$, we have

$$J_m^{\circ}(x) \cong \int_0^x (y^{n-2} - \frac{7}{12} y^n + \dots) dy = \frac{1}{n-1} x^{n-1} - \frac{7}{12(n+1)} x^{n+1} + \dots \quad \text{IV-(56)}$$

and for $x \gg 1$,

$$J_n^{\circ}(x) \cong J_n^{\circ}(\infty) = n \int_0^{\infty} \frac{y^{n-1} dy}{e^y - 1} = n! \sum_{r=1}^{\infty} \frac{1}{r^n} \quad \text{IV-(57)}$$

(e.g. $J(\infty) = 124.4$)

IV-D Calculation of Electron-Phonon Damping Coefficient

The damping coefficient which is contributed by the electron-phonon processes or the electron-phonon collision frequency as it is often called, can be obtained in a straightforward way when we compare the expression for $\langle W \rangle$ obtained in Section IV-C with the corresponding, well known high frequency dispersion formula which is obtained by solving Drude's equation of motion for a free conduction electron.

It is well known that the power expenditure $\langle W \rangle$ for a free electron system is related to the optical conductivity $\sigma(\omega)$ by the relation

$$\frac{E^2 \sigma(\omega)}{2} = n_e \langle W \rangle \quad \text{IV-(58)}$$

where $\langle W \rangle$ is the power expenditure due to one electron per unit time and $\frac{E^2}{2}$ is the energy density of the electromagnetic field. Upon comparing Equation (58) with the expression for $\langle W \rangle$ in Section IV-C, we obtain the relation

$$\sigma_{ep}(\omega) = \frac{1}{4\pi} \frac{\omega_0^2}{\omega^2} R_{ep} \frac{1}{\alpha^5} Z(\mu, \alpha) \quad \text{IV-(59)}$$

where R_{ep} is a constant independent of temperature and frequency. It is determined by the properties of the lattice, and

$$\omega_0 = \left(4\pi \frac{n e^2}{m^*} \right)^{\frac{1}{2}} \quad \text{IV-(60)}$$

where ω_0 is the frequency characteristic of the electron plasma oscillation. ω_0 is generally outside the high frequency limit of the free-electron dispersion spectrum.

At ordinary temperatures, most of the ω -dependence in Equation (59) appears through ω^2 in the denominator as in the case with the high-frequency conductivity of Drude. $Z(\mu, \alpha)$ represents a relatively small variation for changes in ω . According to Equation (50), we have $Z(\mu, \alpha) \sim J_5^0(\alpha)$ when $\mu = 0$. The last three factors in Equation (59) reproduce the well known Grüneisen formula. It also reproduces the d.c. damping coefficient derived by Wilson (1936) when we identify our g and N_p with Wilson's C and Δ^{-1} in the expression for R_{ep} given by

$$R_{ep} = \frac{9\pi^3}{2} \frac{\hbar^2 N_p g^2}{\sqrt{2m^* E_f} MK \Theta} \quad \text{IV-(61)}$$

Thus, by making use of the relation,

$$b_{ep}(\mu, \alpha) = \frac{Z(\mu, \alpha)}{J_5^0(\alpha)} \underset{\omega \rightarrow 0}{\sim} 1 \quad \text{IV-(62)}$$

it is natural for us to identify the last three factors in Equation (59) as a damping coefficient $\Gamma_{ep}(\mu, \alpha)$ similar to its d.c. equivalent Γ_{ep}^0 ,

$$\Gamma_{ep}^0(\alpha) = R_{ep} \frac{1}{\alpha^5} J_5^0(\alpha) \quad \text{IV-(63)}$$

such that

$$\Gamma_{ep}(\mu, \alpha) = \Gamma_{ep}^0(\alpha) b_{ep}(\mu, \alpha) \quad \text{IV-(64)}$$

and

$$\Gamma_{ep}(\mu, \alpha) \underset{\mu \rightarrow 0}{\sim} \Gamma_{ep}(\alpha) \quad \text{IV-(65)}$$

In this respect, $b_{ep}(\mu, \alpha)$ shall be named the quantum correction factor such that

$$\Delta \Gamma_{ep} = \Gamma_{ep}^0(b_{ep} - 1) > 0 \quad \text{IV-(66)}$$

represents the correction for $\omega > 0$.

For the sake of convenience in future applications, we write down $b_{ep}(\mu, \alpha)$ explicitly;

$$b_{ep}(\mu, \alpha) = [J_5^0(\alpha)]^{-1} \frac{e^\mu \sin \mu}{\mu} \left[J_5(\mu, \alpha) - \mu \frac{(e^\mu - 1)^2}{(e^{2\mu} - 1)} J_4(\mu, \alpha) - 2\mu \frac{(e^\mu - 1)^2}{(e^{2\mu} - 1)} K_4(\mu, \alpha) \right] \quad \text{IV-(67)}$$

The optical conductivity $\sigma(\omega)$ in the form of Equation (59) applies only at $\omega^2 \gg \Gamma_{ep}$. A more general form is obtained when $(\omega^2 + \Gamma_{ep}^2)$ is substituted for ω^2 in the denominator to make it consistent with the d.c. properties. We thus have

$$\sigma_{ep}(\mu, \alpha) = \frac{1}{4\pi} \Gamma_{ep}^0 b_{ep}(\mu, \alpha) \left/ \left(\frac{\omega}{\omega_0} \right)^2 \right. + \left(\frac{\Gamma_{ep}^0}{\omega_0} \right)^2 b_{ep}^2(\mu, \alpha) \quad \text{IV-(68)}$$

which gives us the familiar expression for the d.c. conductivity,

$$\sigma_{ep}(\alpha) = \frac{1}{4\pi} \frac{\omega_0^2}{\Gamma_{ep}^0(\alpha)} = \frac{n_e e^2}{m^*} \frac{1}{\Gamma_{ep}^0(\alpha)} \quad \text{IV-(69)}$$

when ω is equated to zero.

A quantity which has essentially the same physical significance as the present $b_{ep}(\mu, \alpha)$ has also been obtained by Gurzhi (1958), and is given by

$$\phi(\mu, \alpha) = \frac{2}{\mu} \frac{1}{\alpha^4} \int_0^\alpha dv \, v^4 \left[\frac{2\mu}{e^{v-1}} + \frac{v-\mu}{e^{v-\mu}-1} - \frac{v+\mu}{e^{v+\mu}-1} \right] \quad \text{IV-(70)}$$

$\phi \approx 1$ when $\mu \ll \alpha \ll 1$. However, Gurzhi's formula fails to reproduce the correct temperature dependence for d.c. resistivity and hence for heat capacity in the limit $\mu \rightarrow 0$ for arbitrary values of α . It agrees identically with the result of the present theory when $\mu \gg \alpha$.

Grüneisen's formula for resistivity is compared with a heat capacity curve in Figure 2, and a good agreement is clearly shown.

A correct theory must be able to reproduce the time-tested classical formulae, be they d.c. properties or optical properties in the classical limit, and the correction

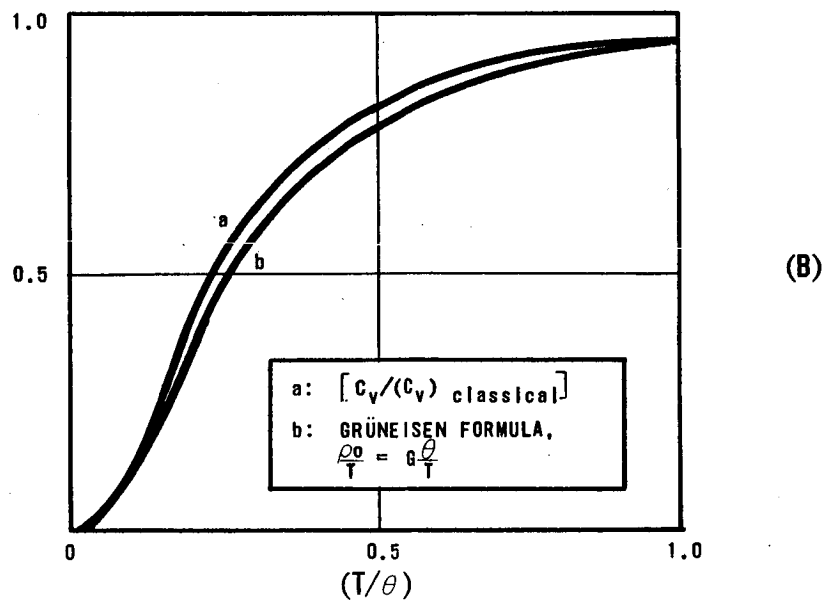
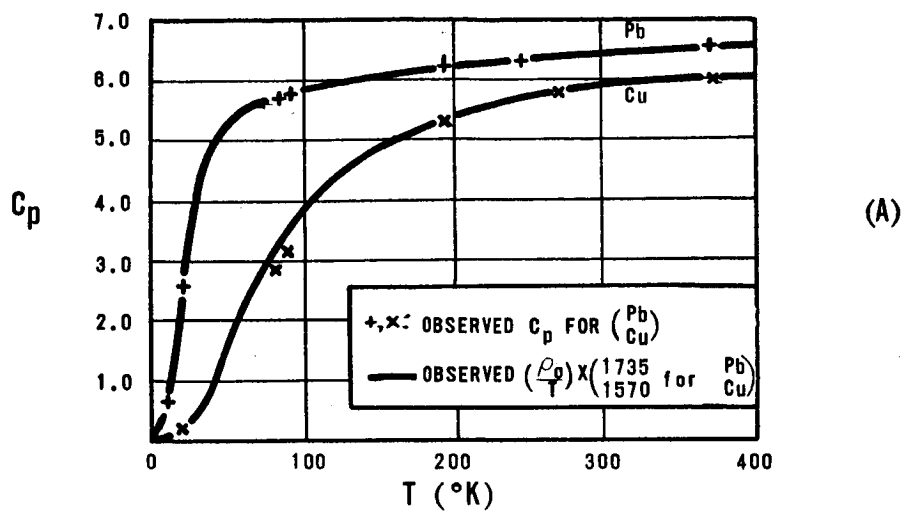


FIGURE 2 Temperature-Dependence of Heat Capacity and Electric Resistance

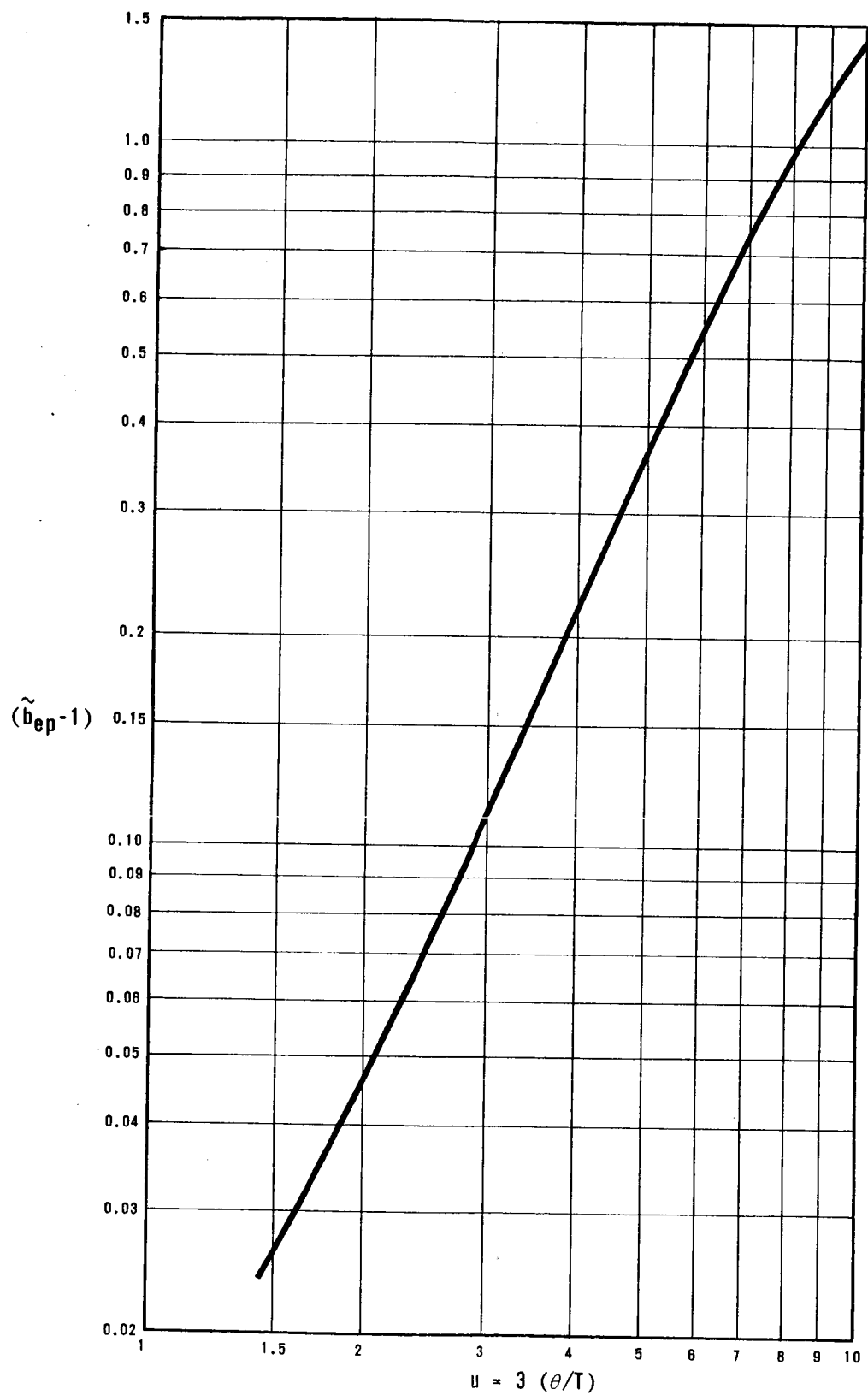


FIGURE 3

Quantum Correction Factor vs
 $\frac{\theta}{T}$ at Short Wavelengths

factor, such as b_{ep} in the present theory, must approach unity identically when $\mu \rightarrow 0$.

IV-E Corrections Due to Electron-Electron Collisions and Impurity Scattering

Contributions to infrared absorption by the processes of electron-electron collisions and impurity scattering have been investigated recently by various authors. Some of the new developments are to be found in the works of the Russian authors, Silin (1958), Pitaevskii (1958) and Gurzhi (1959). Their calculations are based on Landau's theory of Fermi liquids (1957). A metal which is commonly considered to be free of impurities may actually contain impurities in the order of 10^{-4} or less. For such a metal, the impurity contributions can be safely neglected except at very low temperatures. It is well known that even a small impurity content makes an important contribution to the d.c. resistivity at very low temperatures through the "Restwiderstand" of Mathiessen. As for the impurity contributions to various infrared dispersion properties, the investigations in a following chapter reveal that, even at very low temperatures, the impurity contributions can be negligible compared with the contributions by Holstein's mechanism of bulk electron-phonon processes. This is in contrast to common expectations based on our observations of d.c. properties. It results from the important feature

of the present theory that the frequency-dependent damping coefficient $\Gamma_{ep}(\mu, \alpha)$ retains a large value even at very low temperatures when $\mu \gg \alpha$. On the other hand, for an ω which does not satisfy $\mu \gg \alpha$, Γ_{ep} at 0°K, decreases rapidly with increase in wavelength, and thus the impurity and electron-electron collisions become important.

Similar conclusions are reached for the electron-electron processes. It will be shown that the electron-electron collisions are insignificant throughout the free electron spectrum, not only at ordinary temperatures, but also at very low temperatures for many metals. Theoretically, the electron-electron processes make more contributions at higher frequencies and at lower temperatures. Except for transition metals and some multivalent metals, the correction amounts to a small fraction of the contribution by electron-phonon processes in the high frequency region of the free electron spectrum.

Thus, the above conclusions on the significance of the two processes are not in exact agreement with the suggestions by Silin (1958), Pitaevskii (1958), and Gurzhi (1959). They suggest that these two processes may be the only predominant contributions for most cases at low temperatures and in the near infrared, and may be important at room temperature as well for some metals.

For our investigations on the relative magnitudes of the contributions by the three processes, we shall use Gurzhi's formula for the electron-electron collision frequency

$$\Gamma_{ee}(\mu, \alpha) = \Gamma_{ee}^0(\alpha) b_{ee}(\mu) \quad \text{IV-(71)}$$

$$b_{ee}(\mu) = 1 + \left(\frac{\mu}{2\pi} \right)^2 \quad \text{IV-(72)}$$

$\Gamma_{ee}^0(\alpha)$ is the d.c. damping coefficient and is well known to be proportional to $\sim T^2$.

We may write it in the form,

$$\Gamma_{ee}(\alpha) = R_{ee} \frac{1}{\alpha^2} \quad \text{IV-(73)}$$

R_{ee} being a constant having the same dimension as Γ_{ee}^0 . The frequency-dependent factor given by Equation (72) may be considered as a quantum correction factor in the same sense that $b_{ep}(\mu, \alpha)$ has been treated as the quantum correction factor for the electron-phonon collision frequency.

As for the impurity damping, or the electron-impurity scattering frequency as it is often called, it is sufficient to remember that it constitutes a constant, additive quantity Γ_M^0 to the over-all damping coefficient $\Gamma(\mu, \alpha)$, and is independent of both frequency and temperature (or nearly

so). Thus, the over-all damping coefficient, with all of its quantum corrections taken into account, now takes the form,

$$\begin{aligned}\Gamma(\mu, \alpha) &= \Gamma_{ep}(\mu, \alpha) + \Gamma_{ee}(\mu, \alpha) + \Gamma_M^0 \\ &= \Gamma^0(\alpha)b(\mu, \alpha)\end{aligned}\tag{IV-74}$$

$$b(\mu, \alpha) = \frac{\Gamma_{ep}^0(\alpha)b_{ep} + \Gamma_{ee}^0 b_{ee} + \Gamma_M^0}{\Gamma_{ep}^0 + \Gamma_{ee}^0 + \Gamma_M^0}\tag{IV-75}$$

This is to be used in various dispersion relations where the damping coefficient appears. For the reasons that have been explained in most cases it will be satisfactory to consider only the electron-phonon term $\Gamma_{ep}(\mu, \alpha)$. For example, Γ_{ep} alone yields values of low temperature absorptivity of copper and silver at 4.2°K and $\lambda \cong 1 \sim 1.5\mu$ in excellent agreement with the observed values (up to $\sim 2\%$). On the other hand, it is expected that $\Gamma_{ep}(\mu, \alpha)$ will not be sufficient to explain the observed properties of those transition and multivalent metals in which the interband transitions involve a non-zero momentum transfer. Those scattering processes which involve a momentum transfer $|\vec{k}_2 - \vec{k}_1|$ smaller than a certain non-zero minimum do not lead to interband transitions.

Finally, it may be noted that the significance of the electron-electron collision term Γ_{ee}^0 is directly related to the presence of the Umklapp processes. In fact, it has been pointed out (Gurzhi, 1959) that the electron-electron collision term vanishes if the Umklapp process is not present. The relative importance of the Umklapp processes at low temperatures, as compared with the usual phonon mediated processes may be understood in the following manner. Consider that the average momentum transfer in electron-phonon processes decreases like $\sim \left(\frac{T}{\Theta}\right)$ and the density of phonons also decreases rapidly with decrease in the average momentum transfer. The result of these is the rapid decrease of resistivity, $\sim T^5$, as T is decreased to 0°K , while the electron-electron collisions, activated by the Umklapp processes, have the well known $\sim T^2$ -dependence in resistivity. This should, therefore, be even more true in those transition and other multivalent metals in which the interband transitions are very important. A non-zero lower limit in momentum transfer is present for such transitions.

On the other hand, except for the latter special cases, the above statement is not necessarily valid in that range of the optical or infrared spectrum where the quantum correction factor for electron-phonon processes increases sufficiently fast with decrease in temperature to compensate

for decrease in the d.c. quantity Γ_{ep}^0 . For instance, for metals, be they monovalent, multivalent, or transition metals, which involve no non-zero lower limit in momentum transfer, the quantum correction shows the temperature-dependence to be $\sim \frac{1}{T^5}$ while $\Gamma_{ep}(\alpha)$ decreases as $\sim T^5$ when $\hbar\omega \gg K\theta \gg KT$, thus compensating each other exactly.

This is an important consequence of the present theory.

IV-F Calculation of $\epsilon(\mu, \alpha)$

In Section IV-D, we have taken $\sigma(\mu, \alpha)$ in the form,

$$\sigma = \frac{\omega_0^2}{4\pi} \frac{\Gamma}{\omega^2 + \Gamma^2} \quad \text{IV-(68)}$$

where Γ^2 in the denominator comes from Drude's classical equation of motion for free electrons with Γ^0 replaced by $\Gamma(\mu, \alpha)$. Upon solving the same equation, the expression for $\epsilon(\mu, \alpha)$ is obtained in the form,

$$\frac{1-\epsilon}{4\pi} = \frac{\omega_0^2}{4\pi} \frac{1}{\omega^2 + \Gamma^2} \quad \text{IV-(76)}$$

where the denominator has an additional frequency-dependence, besides ω^2 , coming from $b(\mu, \alpha)$ in $\Gamma(\mu, \alpha)$.

Unfortunately, unlike the classical Drude equation, Equation (76) is inconsistent with the Kramers-Kronig relation,

$$\frac{1-\epsilon}{4\pi} = -\frac{2}{\pi} \int_0^{\infty} \frac{\sigma(\omega') d\omega'}{(\omega'^2 - \omega^2)} \quad \text{IV-(77)}$$

We shall calculate $\epsilon(\mu, \alpha)$ from Equation (77) for both cases where (i) $\Gamma_{ep}(\mu, \alpha)$ is the only important term and (ii) $\Gamma_{ee}(\mu, \alpha)$ and Γ_M^0 need be considered. In any case, an exact solution to the integral is difficult due to the complicated structure of ω -dependence in $b_{ep}(\mu, \alpha)$, and a suitable approximation method has to be used.

When $\sigma(\omega)$ contains only Γ_{ep} , we have

$$\begin{aligned} \frac{1-\epsilon}{4\pi} &= -\frac{\omega_0^2}{4\pi^2} \int_{-\infty}^{+\infty} \frac{\Gamma_{ep}^0 b_{ep} d\omega'}{(\omega'^2 + (\Gamma_{ep}^0)^2 b_{ep}^2)(\omega'^2 - \omega^2)} \\ &= -\frac{\omega_0^2}{4\pi^2} \frac{1}{(\Gamma_{ep}^0)^2} \int_{-\infty}^{+\infty} \frac{b_{ep}(x) dx}{(x^2 + [b_{ep}(x)]^2)(x^2 - y^2)} \end{aligned} \quad \text{IV-(78)}$$

where $x = \left(\frac{\omega'}{\Gamma_{ep}^0}\right)$ and $y = \left(\frac{\omega}{\Gamma_{ep}^0}\right)$, and where we have used

$$b_{ep}(\mu, \alpha) \equiv b_{ep}(-\mu, \alpha) \quad \text{IV-(79)}$$

In order to investigate the property of $(1-\epsilon)$ in the two extreme limits, $\omega^2 \gg (\Gamma_{ep}^0)^2$ and $\omega \rightarrow 0$, we use the relation

$$\frac{1}{(x^2 + b^2)(x^2 - y^2)} = \frac{(-1)}{(y^2 + b^2)} \left[\frac{1}{x^2 + b^2} - \frac{1}{x^2 - y^2} \right]$$

and we have

$$\begin{aligned} \frac{1-\epsilon}{4\pi} = \frac{\omega_0^2}{4\pi^2} \frac{1}{(\Gamma_{ep}^0)^2} & \left[\int_{-\infty}^{+\infty} \frac{b(x) dx}{(y^2 + b^2)(x^2 + b^2)} \right. \\ & \left. - \int_{-\infty}^{+\infty} \frac{b(x) dx}{(x^2 - y^2)(y^2 + b^2)} \right] \end{aligned} \quad \text{IV-(80)}$$

where the subscript ep has been dropped for convenience, and b^2 's appearing in the integrand are all functions of x and not of y .

Before attempting to solve Equation (80), it may be remembered that $b_{ep}(x)$ is a very slowly varying function of x throughout the entire spectral range except when the temperature is such as to give $1 \ll \mu \ll \alpha$ in the very far infrared, and that $b_{ep}(\mu, \alpha)$ is $\sim 0(1)$, being always greater than unity for $\omega > 0$.

In the limit of $\mu \gg \alpha$, Equation (80) now becomes

$$\frac{1-\epsilon}{4\pi} = \frac{\omega_0^2}{4\pi} \frac{\delta_{ep}^{\sim}}{\omega^2} \quad \text{IV-(81)}$$

where

$$\delta_{ep}^{\sim} = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{b(x)}{(x^2 + b^2)} dx = \frac{8}{\omega_0^2} \int_0^{\infty} \sigma(\omega) d\omega \quad IV-(82)$$

In obtaining Equation (82), it was assumed that $b(x) \equiv b(-x)$ and that $b(x)$ does not have a singularity in the complex x -plane.

We notice in Equation (82) that, when $\sigma(\omega)$ satisfies the sum rule

$$\frac{2}{\pi} \int_0^{\infty} \sigma(\omega) d\omega = \frac{\omega_0^2}{4\pi} \quad IV-(83)$$

we simply have $\delta_{ep}^{\sim} = 1$.

In the limit of $\mu \ll 1$, we obtain from Equation (80),

$$\frac{1-\epsilon_0}{4\pi} = \frac{\omega_0^2}{4\pi} \frac{1}{(\Gamma_{ep})^2} \frac{\delta_{ep}^{\sim}}{\beta^2} \quad IV-(84)$$

where

$$\frac{\delta_{ep}^{\sim}}{\beta^2} = \frac{1}{\pi} \left(\int_{-\infty}^{+\infty} \frac{dx b(x)}{(\eta + b^2)(x^2 + b^2)} - \int_{-\infty}^{+\infty} \frac{dx b(x)}{(x^2 - \eta)(\eta + b^2)} \right)$$

The presence of η in the integrands implies that, in solving the integrals by a contour in complex x -space, the zeros of $b(x)$ must be taken as the zeros of the integrands and not as singularities of the integrands, for all $\eta \gtrsim 0$. In this case, it is easily shown that the second integral vanishes, and we have

$$\frac{\delta_{ep}^{\sim}}{\bar{\beta}^2} = \frac{1}{\pi} \left(\int_{-\infty}^{+\infty} \frac{dx \, b(x)}{(x^2 + b^2)(b^2 + \eta)} \right)_{\eta \approx 0} \quad \text{IV-(85)}$$

The integrand is taken to vanish at the zeros of $b(x)$.

Upon comparing Equations (81) and (84), we construct one possible form of $(1-\epsilon)$, namely

$$\frac{1-\epsilon}{4\pi} = \frac{\omega_0^2}{4\pi} \frac{\delta_{ep}}{\omega^2 + (\Gamma_{ep}^0)^2 \bar{\beta}^2} \quad \text{IV-(86)}$$

where δ_{ep} and $\bar{\beta}$ may or may not depend on ω , and if δ_{ep} is independent of ω , we simply have

$$\delta_{ep} = \delta_{ep}^{\sim} = 1$$

Taking δ_{ep} and β^2 to be independent of ω is essentially equivalent to evaluating the integral (28) by replacing b^2 of denominator by a parameter $\bar{\beta}^2$. In fact, such an approximation is reasonably well justified for $b_{ep}(x)$ is a very slowly varying function of ω for all $-\infty < x < +\infty$, except for the case of $1 \lesssim \mu \ll \alpha$ (which can occur at very low temperature and in the very far infrared limit). The parameter which best approximates the integrand may be found by a successive approximation, solving the identity equation

$$\bar{\beta}(\alpha) = b_{ep}(i \bar{\beta} \mu_o, \alpha) \quad \text{IV-(87)}$$

$$: \mu_o = \left(\frac{\Gamma_{ep}^o}{KT} \right)$$

where $\bar{\beta}(\alpha)$ is independent of ω .

By such an approximation, Equation (78) is readily solved, and we obtain

$$\frac{1-\epsilon}{4\pi} \approx \frac{\omega_o^2}{4\pi} \frac{1}{\omega^2 + (\Gamma_{ep}^o)^2 \beta^2} \quad \text{IV-(88)}$$

which applies to all temperatures and ω 's except for the case of $1 \ll \mu \ll \alpha$ in which b_{ep} can be a very rapidly varying function of ω although the over-all magnitude of $(\Gamma_{ep}^o b_{ep})$ is generally very small.

It is seen that Equation (88) is identical with Equation (86) when we put $\delta_{ep} = 1$ and take $\bar{\beta}$ as a frequency-independent parameter. Further, the sum rule Equation (83) is automatically satisfied.

The said statement that $b_{ep}(x)$ has zeros but no singularities in the complex x - or $\bar{\mu}$ -plane can be understood upon examining the complete expression of $b_{ep}(\bar{\mu}, \alpha)$ in the complex $\bar{\mu}$ -plane. From Section IV-C, we have the following expression for $b_{ep}(\bar{\mu})$;

$$b(\bar{\mu}) = b^I(\bar{\mu}) + i b^{II}(\bar{\mu})$$

$$\bar{\mu} = \mu_1 + i\mu_2$$

$$\begin{aligned}
 b^I(\bar{\mu}) = & \frac{1}{2} \left[\frac{\left(\mu_1 (e^{2\mu_1} \cos 2\mu_2 - 1) + \mu_2 e^{2\mu_1} \sin 2\mu_2 \right)}{\mu_1^2 + \mu_2^2} \left\{ J_5^I(\bar{\mu}) \right. \right. \\
 & + J_5^{II}(\bar{\mu}) \frac{[\mu_2 (e^{2\mu_1} \cos 2\mu_2 - 1) - \mu_1 e^{2\mu_1} \sin 2\mu_2]}{[\mu_1 (e^{2\mu_1} \cos 2\mu_2 - 1) + \mu_2 e^{2\mu_1} \sin 2\mu_2]} \left. \right\} \\
 & - \left((e^{\mu_1} \cos \mu_2 - 1)^2 - e^{2\mu_1} \sin \mu_2 \right) \left\{ J_4^I(\bar{\mu}) + 2K_4^I(\bar{\mu}) \right. \\
 & + \frac{2e^{\mu_1} \sin \mu_2 (e^{\mu_1} \cos \mu_2 - 1)}{[(e^{\mu_1} \cos \mu_2 - 1)^2 - e^{2\mu_1} \sin \mu_2]} \\
 & \left. \left. \times \left(J_4^{II}(\bar{\mu}) + 2K_4^{II}(\bar{\mu}) \right) \right\} \right]
 \end{aligned} \tag{IV-89}$$

where we have put

$$J_n(\bar{\mu}, \alpha) = J_n^I(\bar{\mu}) + i J_n^{II}(\bar{\mu})$$

$$K_n(\bar{\mu}, \alpha) = K_n^I(\bar{\mu}) + i K_n^{II}(\bar{\mu})$$

$$J_n^I(\bar{\mu}) = J_n^I(-\bar{\mu}) = \int_0^\alpha y^n dy \frac{[(e^y + e^{-y})e^{\mu_1} \cos \mu_2 - e^{2\mu_1} \cos 2\mu_2 - 1]}{D(\bar{\mu}, y)}$$

$$J_n^{II}(\bar{\mu}) = -J_n^{II}(-\bar{\mu}) = \int_0^\alpha y^n dy \frac{[e^{2\mu_1} \sin 2\mu_2 - (e^y + e^{-y})e^{\mu_1} \sin \mu_2]}{D(\bar{\mu}, y)}$$

$$K_n^I(\bar{\mu}) = K_n^I(-\bar{\mu}) = \int_0^\alpha y^n dy \frac{[(e^y + e^{-y})e^{\mu_1} \cos \mu_2 - e^{2\mu_1} \cos \mu_2 - 1]}{(e^y - 1) D(\bar{\mu}, y)}$$

$$K_n^{II}(\bar{\mu}) = K_n^{II}(-\bar{\mu}) = \int_0^\alpha y^n dy \frac{[e^{2\mu_1} \sin 2\mu_2 - (e^y + e^{-y})e^{\mu_1} \sin \mu_2]}{(e^y - 1) D(\bar{\mu}, y)} \quad \text{IV-(90)}$$

where

$$D(\bar{\mu}, y) = [(e^y - e^{\mu_1} \cos \mu_2)^2 + e^{2\mu_1} \sin^2 \mu_2] \\ \times [(e^{\mu_1} \cos \mu_2 - e^{-y})^2 + e^{2\mu_1} \sin^2 \mu_2]$$

Similarly, the expression for $b^{II}(\bar{\mu})$ is obtained upon replacing (J_n^I, K_n^I) and (J_n^{II}, K_n^{II}) by (J_n^{II}, K_n^{II}) and $(-J_n^I, +K_n^I)$, respectively.

A detailed study of the Expressions (89) and (90) shows that $b(\bar{\mu})$ has no singularity, but has an infinite number of zeros on the real axis of the μ -plane at

$$\mu = \pm i \frac{n}{2} \pi$$

$$n = 1, 2, 3, \dots$$

This implies that in obtaining the solution (88), we must make sure that only those values of $\bar{\beta}$ which meet the condition

$$\begin{aligned} \mu_0 \bar{\beta} &\neq \frac{n}{2} \pi \\ &: n = 1, 2, 3, 4, \dots \end{aligned} \quad \text{IV-(91)}$$

are considered. We further notice, in Equation (87) which defines $\bar{\beta}$, that any $\bar{\beta}$ which is found from Equation (87) satisfies the condition (91) automatically. The solution to Equation (87) is obtained upon putting $\mu_1 = 0$ and $\mu_2 = \mu_0 \bar{\beta}$ into Equations (89) and (90). We thus have

$$\begin{aligned} \bar{\beta}(\alpha) &= b_{ep}(i\mu_0 \bar{\beta}) \\ &= \frac{1 + \sin^2(\mu_0 \bar{\beta})}{\mu_0 \bar{\beta} J_5^0(\alpha)} \left[\tan(\mu_0 \bar{\beta}) J_5^I(\mu_0 \bar{\beta}) \right. \\ &\quad \left. + (\mu_0 \bar{\beta}) \frac{1 - \cos(\mu_0 \bar{\beta})}{\cos(\mu_0 \bar{\beta})} (J_4^I + 2K_4^I) \right] \end{aligned} \quad \text{IV-(92)}$$

where we have used the relation

$$\frac{J_n^{II}(i\mu_0 \bar{\beta})}{J_n^I(i\mu_0 \bar{\beta})} = \frac{K_n^{II}(i\mu_0 \bar{\beta})}{K_n^I(i\mu_0 \bar{\beta})} = -2 \tan(\mu_0 \bar{\beta}) \quad \text{IV-(93)}$$

and

$$J_n^I(i\mu_0\bar{\beta}) = \int_0^\alpha \frac{y^n dy [(e^y - \cos\mu_0\bar{\beta})(\cos\mu_0\bar{\beta} - e^{-y}) + \sin^2(\mu_0\bar{\beta})]}{[(e^y - \cos\mu_0\bar{\beta})^2 + \sin^2\mu_0\bar{\beta}][\cos\mu_0\bar{\beta} - e^{-y})^2 + \sin^2(\mu_0\bar{\beta})]}$$

$$K_n^I(i\mu_0\bar{\beta}) = \int_0^\alpha \frac{y^n dy [---]}{(e^y - 1)[---][---]} \quad \text{IV-(94)}$$

Evaluations of $\bar{\beta}(\alpha)$ in the two limiting cases, $\alpha \gg 1$ and $\alpha \ll 1$, are simplified considerably.

In the limit $\alpha \gg 1$, we have

$$J_n^I \cong \cos(\mu_0\bar{\beta}) n! \left[1 - \sum_{m=1}^{\infty} \frac{m}{(m+2)^{n+1}} \cos^{m+1}(\mu_0\bar{\beta}) \right]$$

IV-(95)

$$K_n^I \cong n! \cos(\mu_0\bar{\beta}) \left[\frac{1}{2^{n+1}} + \frac{1}{3^{n+1}} + \sum_{m=2}^{\infty} \frac{1}{(m+2)^{n+1}} \left(1 - \sum_{s=1}^{m-1} s \cos^{s+1}(\mu_0\bar{\beta}) \right) \right]$$

For $n=4$ and $n=5$, it is safe to take only the first terms of Equation (95), and we have

$$J_5^I \sim 120 \cos(\mu_0\bar{\beta}) \quad ; \quad J_4^I \sim 24 \cos(\mu_0\bar{\beta})$$

$$K_4^I \sim \frac{3}{4} \cos(\mu_0\bar{\beta}) \quad \text{IV-(96)}$$

$$J_5^0 \sim 124$$

On the other hand, in the limit $\alpha \ll 1$, it easily follows that

$$I_n^I \cong \frac{\alpha^{n+1}}{8(n+1)} \frac{\cos(\mu_0 \bar{\beta})}{\sin^4\left(\frac{\mu_0 \bar{\beta}}{2}\right)}$$

$$K_n^I \cong \frac{\alpha^n}{8n} \frac{\cos(\mu_0 \bar{\beta})}{\sin^4\left(\frac{\mu_0 \bar{\beta}}{2}\right)} \quad \text{IV-(97)}$$

$$: \mu_0 \bar{\beta} \neq \frac{m\pi}{2} \quad (m = 0, 1, 2, \dots)$$

$$J_5^0 \cong \frac{1}{4} \alpha^4$$

Thus, the identity Equation (92) is reduced to the following two corresponding to the limits, $\alpha \gg 1$ and $\alpha \ll 1$, respectively.

$$\frac{(\mu_0 \bar{\beta})^2}{\mu_0} \cong (1 + \sin^2 \mu_0 \bar{\beta}) \left[\sin(\mu_0 \bar{\beta}) + \frac{(\mu_0 \bar{\beta})}{2} (1 - \cos \mu_0 \bar{\beta}) \right] \quad \text{IV-(98)}$$

$$\frac{(\mu_0 \bar{\beta})^2}{\mu_0} \cong \frac{(1 + \sin^2 \mu_0 \bar{\beta})}{4 \sin^4\left(\frac{\mu_0 \bar{\beta}}{2}\right)} \left[\frac{1}{3} \alpha^2 \sin(\mu_0 \bar{\beta}) + \frac{\mu_0 \bar{\beta}}{2} (1 - \cos \mu_0 \bar{\beta}) \right] \quad \text{IV-(99)}$$

These equations are in a numerically solvable form provided that we know the value of μ_0 and hence $\Gamma_{ep}^0(\alpha)$. The solutions to these equations may be obtained with the help of our formula for $\Gamma_{ep}^0(\alpha)$. According to Equation (63), it is seen that

$$\mu_0 \sim \frac{1}{\alpha^4} \ll 1$$

in the limit $\alpha \gg 1$, and the only possible solution to

Equation (98) exists when $(\mu_0 \bar{\beta}) \ll 1$. Thus we find

$$\bar{\beta} \approx 1 : \alpha \gg 1 \quad \text{IV-(100)}$$

On the other hand, if $\alpha \ll 1$ (high temperature), Equation (63) tells us that $\Gamma_{ep} \sim T$ and $\mu_0 \sim \text{constant}$ such that

$$\mu_0 \sim 0(1)$$

According to Equation (85), $b(x)$ and $\bar{\beta}$ are $\sim 0(1)$.

We thus find, from Equation (99),

$$\bar{\beta} \approx \frac{1 + \sin^2(\mu_0 \bar{\beta})}{4 \sin^2 \left(\frac{\mu_0 \bar{\beta}}{2} \right)} : \alpha \ll 1 \quad \text{IV-(101)}$$

where $(\mu_0 \bar{\beta}) \sim 0(1) < \frac{\pi}{2}$.

According to the result shown in Equation (100), the denominator in the dispersion formula for $(1-\epsilon)$ is to be taken as

$$\left(\frac{1}{\omega^2 + (\Gamma_{ep}^0)^2} \right)$$

when $\alpha \gg 1$, while that of $\sigma(\omega)$ is to be taken as

$$\frac{1}{\omega^2 + (\Gamma_{ep}^0)^2 (\tilde{b})^2}$$

with $\tilde{b} > 1$.

In the forthcoming applications of the theory to practical cases, we shall in general take $\bar{\beta}$ as a temperature-dependent parameter to be determined by fitting theoretical equations to experimental curves, while b_{ep} is calculated theoretically.

IV-G Calculation of $\epsilon(\mu, \alpha)$ with the Electron-Electron Collisions and Impurity Effects taken into Account

We have thus far considered only that part of dispersion which is contributed by the bulk electron-phonon processes. For a more general calculation of $\epsilon(\mu, \alpha)$, we must use the formula (74) and (75) in the Kramers-Kronig relation. Aside from this, the calculational procedure is similar to that of Section IV-E.

For the sake of convenience, we define the following notations:

$$\bar{\Omega}_0(\alpha) = \left(\Gamma_{ep}^0 \bar{\beta}_{ep} + \Gamma_{ee}^0 + \Gamma_M^0 \right) ; \Omega_0 = \left(\Gamma_{ep}^0 b_{ep} + \Gamma_{ee}^0 + \Gamma_M^0 \right)$$

$$\left[\Omega_{ee}(\alpha) \right]^{-1} = \left(\frac{\hbar \beta}{2\pi} \right)^2 \Gamma_{ee}^0(\alpha) \quad \text{IV-(102)}$$

$$\bar{\Omega}_{\pm}^2 = -\frac{1}{2} \Omega_{ee}^2 \left\{ \left[1 + 4 \frac{\bar{\Omega}_0}{\Omega_{ee}} \right]^{\frac{1}{2}} \pm \left[1 + 2 \frac{\bar{\Omega}_0}{\Omega_{ee}} \right] \right\}$$

Then, the dispersion denominator in $\sigma(\mu, \alpha)$ can be put into the form,

$$(\omega^2 + \Gamma^2) = \frac{(\omega^2 + \bar{\Omega}_+^2)(\omega^2 + \bar{\Omega}_-^2)}{\Omega_{ee}^2} \quad \text{IV-(103)}$$

and we have

$$\sigma(\mu, \alpha) = \frac{\omega_0^2}{4\pi} \frac{\Omega_{ee} \left(\Omega_0(\omega) + \frac{\omega^2}{\Omega_{ee}} \right)}{(\omega^2 + \Omega_+^2)(\omega^2 + \Omega_-^2)} \quad \text{IV-(104)}$$

where Ω 's without bars represent quantities of Equation (102) with $\bar{\beta}_{ep}$ replaced by $b_{ep}(\mu, \alpha)$, where $\bar{\beta}_{ep}$ is a temperature-dependent but frequency-independent parameter similar to $\bar{\beta}$ assumed in Section IV-E. A close examination of $\bar{\Omega}_{\pm}$ in Equation (102) shows that

$$\bar{\Omega}_{\pm}, \Omega_{\pm} > 0$$

In solving the Kramers-Kronig relation, we shall again use $\bar{\beta}_{ep}$ in place of b_{ep} in the denominators. This approximation is just as much valid as the same approximation that was adopted in Section IV-E. Then we have

$$\begin{aligned} \frac{1-\epsilon}{4\pi} &= - \frac{\omega_0^2}{4\pi} \Omega_{ee}^2 \int_{-\infty}^{+\infty} d\omega' \frac{\left(\Omega_0(\omega') + \frac{\omega'^2}{\Omega_{ee}} \right)}{(\omega'^2 + \Omega_+^2)(\omega'^2 + \Omega_-^2)(\omega'^2 - \omega^2)} \\ &\approx - \frac{\omega_0^2}{4\pi} \Omega_{ee}^2 \int_{-\infty}^{+\infty} d\omega' \frac{\left(\Omega_0(\omega') + \frac{\omega'^2}{\Omega_{ee}} \right)}{(\omega'^2 + \bar{\Omega}_+^2)(\omega'^2 + \bar{\Omega}_-^2)(\omega'^2 - \omega^2)} \end{aligned} \quad \text{IV-(105)}$$

This may be solved by taking the contour integral in the upper half of the complex ω' -plane enclosing the poles on the $\bar{\Omega}$ -axis at $\omega' = +i\bar{\Omega}_+$ and $+i\bar{\Omega}_-$, the semi-circular

arc extending from $\omega' = +\infty$ to $+i\infty$ and then to $-\infty$, and the contour being indented above the real points at $\omega' = \pm \omega$.

We thus obtain

$$\frac{1-\epsilon}{4\pi} \approx \frac{\omega_o^2}{4\pi} \frac{\Omega_{ee}^2}{(\bar{\Omega}_+^2 - \bar{\Omega}_-^2)} \times \left[\frac{\left(\frac{\Omega_o [i\bar{\Omega}_-]}{\bar{\Omega}_-} - \frac{\bar{\Omega}_-}{\Omega_{ee}} \right)}{\omega^2 + \bar{\Omega}_-^2} - \frac{\left(\frac{\Omega_o [i\bar{\Omega}_+]}{\bar{\Omega}_+} - \frac{\bar{\Omega}_+}{\Omega_{ee}} \right)}{\omega^2 + \bar{\Omega}_+^2} \right] \quad \text{IV-(106)}$$

In general, we have

$$\frac{\Omega_o}{\Omega_{ee}} \ll 1 \quad ; \quad \frac{\omega}{\Omega_{ee}} \ll 1 \quad \text{IV-(107)}$$

for all ω in the free electron region of spectrum, and thus

$$\bar{\Omega}_{\pm} \approx \left(\frac{\Omega_{ee}}{\bar{\Omega}_o} \right)$$

$$(\bar{\Omega}_+^2 - \bar{\Omega}_-^2) \approx \Omega_{ee}^2$$

so that Equation (106) can be reduced to the form,

$$\frac{1-\epsilon}{4\pi} \approx \frac{\omega_o}{4\pi} \frac{1}{\omega^2 + \bar{\Omega}_o^2} \quad ; \quad \frac{\Omega_o (i\bar{\Omega}_o)}{\bar{\Omega}_o} = 1 \quad \text{IV-(108)}$$

$$\sigma(\mu, \alpha) = \frac{\omega_0^2}{4\pi} \frac{\Omega_{ee} \left(\Omega_0(\omega) + \frac{\omega^2}{\Omega_{ee}} \right)}{(\omega^2 + \Omega_+^2)(\omega^2 + \Omega_-^2)} \quad \text{IV-(104)}$$

where Ω 's without bars represent quantities of Equation (102) with $\bar{\beta}_{ep}$ replaced by $b_{ep}(\mu, \alpha)$, where $\bar{\beta}_{ep}$ is a temperature-dependent but frequency-independent parameter similar to $\bar{\beta}$ assumed in Section IV-E. A close examination of $\bar{\Omega}_{\pm}$ in Equation (102) shows that

$$\bar{\Omega}_{\pm}, \Omega_{\pm} > 0$$

In solving the Kramers-Kronig relation, we shall again use $\bar{\beta}_{ep}$ in place of b_{ep} in the denominators. This approximation is just as much valid as the same approximation that was adopted in Section IV-E. Then we have

$$\begin{aligned} \frac{1-\epsilon}{4\pi} &= -\frac{\omega_0^2}{4\pi} \Omega_{ee}^2 \int_{-\infty}^{+\infty} d\omega' \frac{\left(\Omega_0(\omega') + \frac{\omega'^2}{\Omega_{ee}} \right)}{(\omega'^2 + \Omega_+^2)(\omega'^2 + \Omega_-^2)(\omega'^2 - \omega^2)} \\ &\approx -\frac{\omega_0^2}{4\pi} \Omega_{ee}^2 \int_{-\infty}^{+\infty} d\omega' \frac{\left(\Omega_0(\omega') + \frac{\omega'^2}{\Omega_{ee}} \right)}{(\omega'^2 + \bar{\Omega}_+^2)(\omega'^2 + \bar{\Omega}_-^2)(\omega'^2 - \omega^2)} \end{aligned} \quad \text{IV-(105)}$$

This may be solved by taking the contour integral in the upper half of the complex ω' -plane enclosing the poles on the $\bar{\Omega}$ -axis at $\omega' = +i\bar{\Omega}_+$ and $+i\bar{\Omega}_-$, the semi-circular

arc extending from $\omega' = +\infty$ to $+i\infty$ and then to $-\infty$, and the contour being indented above the real points at $\omega' = \pm \omega$.

We thus obtain

$$\frac{1-\epsilon}{4\pi} \approx \frac{\omega_o^2}{4\pi} \frac{\Omega_{ee}^2}{(\bar{\Omega}_+^2 - \bar{\Omega}_-^2)} \times \left[\frac{\left(\frac{\Omega_o[i\bar{\Omega}_-]}{\bar{\Omega}_-} - \frac{\bar{\Omega}_-}{\Omega_{ee}} \right)}{\omega^2 + \bar{\Omega}_-^2} - \frac{\left(\frac{\Omega_o[i\bar{\Omega}_+]}{\bar{\Omega}_+} - \frac{\bar{\Omega}_+}{\Omega_{ee}} \right)}{\omega^2 + \bar{\Omega}_+^2} \right] \quad \text{IV-(106)}$$

In general, we have

$$\frac{\Omega_o}{\Omega_{ee}} \ll 1 \quad ; \quad \frac{\omega}{\Omega_{ee}} \ll 1 \quad \text{IV-(107)}$$

for all ω in the free electron region of spectrum, and thus

$$\bar{\Omega}_{\pm} \approx \left(\frac{\Omega_{ee}}{\bar{\Omega}_o} \right)$$

$$(\bar{\Omega}_+^2 - \bar{\Omega}_-^2) \approx \Omega_{ee}^2$$

so that Equation (106) can be reduced to the form,

$$\frac{1-\epsilon}{4\pi} \approx \frac{\omega_o}{4\pi} \frac{1}{\omega^2 + \bar{\Omega}_o^2} \quad ; \quad \frac{\Omega_o(i\bar{\Omega}_o)}{\bar{\Omega}_o} = 1 \quad \text{IV-(108)}$$

where Ω_0 ($i\tilde{\Omega}_0$) is real since $b_{ep}(ix) = b_{ep}(-ix)$ and the parameter $\tilde{\beta}_{ep}$ is found from the identity equation,

$$\tilde{\beta} = b_{ep}(i\zeta)$$

IV-(109)

$$\zeta = \hbar \tilde{\beta} (\Gamma_{ep}^0 \tilde{\beta} + \Gamma_{ee}^0 + \Gamma_M^0)$$

which becomes identical to Equation (92) in Section IV-F when Γ_{ee}^0 and Γ_M^0 are small compared with the electron-phonon contribution. We found previously that, at low temperatures ($\alpha \gg 1$), we have

$$\Gamma_{ep}^0 \ll 1 ; \quad \tilde{\beta}_{ep} \approx 1$$

while $\Gamma_{ee}^0(\alpha)$ decreases relatively slowly, like $\sim T^2$, as T is decreased and Γ_M^0 is the constant, "Restwiderstand" term, so that, in this limit,

$$\zeta \approx \hbar \tilde{\beta} (\Gamma_{ee}^0 + \Gamma_M^0) = \zeta_0 \quad \text{IV-(110)}$$

independent of $\tilde{\beta}$. Therefore, fortunately enough, we need not be concerned with evaluating $\tilde{\beta}$ at all at low temperatures and $(1-\epsilon)$ is simply given by

$$\frac{1-\epsilon}{4\pi} \approx \frac{\omega_0^2}{4\pi} \frac{1}{\omega^2 + (\Gamma_{ee}^0 + \Gamma_M^0)^2} : \alpha \gg 1 \quad \text{IV-(111)}$$

On the other hand, at not too low temperatures, Γ_{ee}^0 and Γ_M^0 are both much smaller than $\Gamma_{ep}^0 \bar{\beta}$ so that the expression for $(1-\epsilon)$ is nearly the same as that obtained in Section IV-F.

Similarly, the properties indicated in Equation (107) enable us to write down σ in a reduced form,

$$\sigma = \frac{\omega_o^2}{4\pi} \frac{\Omega_o(\mu, \alpha)}{\omega^2 + [\Omega_o(\mu, \alpha)]^2} \left(1 + \frac{\omega^2}{\Omega_o \Omega_{ee}} \right) \quad \text{IV-(112)}$$

which is to be applied whenever Equation (108) is applicable.

It must be remembered that the electron-phonon part of $\Omega_o(\mu, \alpha)$ in Equation (112) is not necessarily smaller than $(\Gamma_{ee}^0 + \Gamma_M^0)$ because $b_{ep}(\mu, \alpha)$, instead of $\bar{\beta}$, is multiplied to $\Gamma_{ep}^0(\alpha)$ in Ω_o . In fact, it is found that the rapid decrease of Γ_{ep}^0 (i.e., like $\sim T^5$) with decrease in T is exactly compensated by the $\sim \frac{1}{T^5}$ -dependence of $b_{ep}(\mu, \alpha)$ in certain parts of the free electron spectrum.

Chapter V

Absorptivity, Reflectivity, Optical Size of Conduction Electrons, and Other Properties of Metals

V-A Basic Formulae from Chapter IV

The formulae for optical conductivity $\sigma(\omega)$ and dielectric constant $\epsilon(\omega)$ were obtained in the preceding chapter, first by considering the contribution of only the electron-phonon processes, and second, for the more general case where electron-electron collisions and impurity scattering also need to be taken into account.

In the applications that follow, we shall use the general formulae obtained for the second case.

When the quantity $\left(\frac{\omega^2}{\Omega_{ee}^2} \right)$ is not neglected, the expression for $\sigma(\omega)$ and $\epsilon(\omega)$ take the form

$$\sigma(\omega) = \frac{\omega_0^2}{4\pi} \frac{\Omega_0}{\Omega_1^2} G_\sigma(\omega) \quad \text{V-(1)}$$

$$[1 - \epsilon(\omega)] = \frac{\omega_0^2}{\Omega_2^2} G_\epsilon(\omega) \quad \text{V-(2)}$$

where

$$\Omega_1^2 = \omega^2 + \Omega_0^2$$

$$\Omega_2^2 = \omega^2 + \bar{\Omega}_0^2$$

$$G_\sigma(\omega) = \frac{1 + \frac{\omega^2}{\Omega_0 \Omega_{ee}}}{1 + \left(\frac{\omega}{\Omega_{ee}} \right)^2}$$

$$G_{\epsilon}(\omega) = \frac{1 + 2 \left(\frac{\omega}{\Omega_{ee}} \right)^2}{1 + \left(\frac{\omega}{\Omega_{ee}} \right)^2}$$

V-(3)

$$\Omega_0 = \Gamma_{ep}^0(\alpha) b_{ep}(\mu, \alpha) + \Gamma_{ee}^0(\alpha) + \Gamma_M^0$$

$$\bar{\Omega}_0 = \Gamma_{ep}^0(\alpha) \bar{b}_{ep}(\alpha) + \Gamma_{ee}^0(\alpha) + \Gamma_M^0$$

The multiplicative factors, G_{σ} and G_{ϵ} , are corrections due to electron-electron collisions and, in general, are of the order of unity. The entire temperature-dependence in Equations (1) and (2) appears only through Ω_0 and $\bar{\Omega}_0$. Only Ω_0 shows frequency dependence through the term $b_{ep}(\mu, \alpha)$. The formulae (1) and (2) are more general than Equations IV-(112) and IV-(108), since the latter two neglect $\left(\frac{\omega}{\Omega_{ee}} \right)^2$ which is small compared to unity. In general, $\left(\frac{\omega}{\Omega_{ee}} \right)^2$ is small compared to unity throughout the entire free-electron spectrum (i.e., $\lambda \gtrsim 0.5 \sim 1.0 \mu$) for all temperatures, so that

$$G_{\epsilon}(\omega) \approx 1$$

V-(4)

$$G_{\sigma}(\omega) \approx \left(1 + \frac{\omega^2}{\Omega_0 \Omega_{ee}} \right)$$

In order to justify this statement, let us compute $\left(\frac{\omega}{\Omega_{ee}} \right)^2$ for a metal which shows a relatively large contribution of electron-electron collisions, and see at what wavelength the relations of (4) are not valid. For this purpose, we write $\Gamma_{ee}^0(\alpha)$ as

$$\Gamma_{ee}^0(\alpha) = R_{ee} \frac{1}{\alpha^2} \quad \text{V-(5)}$$

where R_{ee} is independent of both T and ω . Then, we have

$$\left(\frac{\omega}{\Omega_{ee}}\right)^2 = \frac{3.84 \times 10^{-18}}{\lambda^2} \left(\frac{R_{ee}}{\Theta^2}\right)^2 \quad \text{V-(6)}$$

$$: \lambda = \frac{2\pi c}{\omega} (\mu)$$

For most metals, the values of R_{ee} range from $\sim 10^{10} \text{ sec}^{-1}$ to $\sim 10^{12} \text{ sec}^{-1}$ while Θ is of the order of $\sim 10^2$ ($^{\circ}\text{K}$). Therefore, for $\Theta = 300^{\circ}\text{K}$ and $R_{ee} = 10^{12} \text{ sec}^{-1}$, the wavelength which gives $\left(\frac{\omega^2}{\Omega_{ee}^2}\right) \approx 0.1$ ($\sim 10\%$ correction) is found as $0.2 \sim 0.3 \mu$, which is already outside the free electron region of the spectrum. On the other hand, $\left(\frac{\omega^2}{\Omega_0 \Omega_{ee}}\right)$ is not necessarily small, since we have $\left(\frac{\omega}{\Omega_0}\right) \gg 1$ in the near infrared.

In order to predict values of various dispersion properties such as the optical constants, absorptivity and reflectivity, etc., at different temperature by knowing the values of these quantities at one temperature, it is sufficient to specify the temperature-dependence of Ω_0 and $\bar{\Omega}_0$ in addition to the values of the constant parameters entering in Ω_0 , $\bar{\Omega}_0$ and Ω_{ee} . At not too low temperatures, Ω_0 and $\bar{\Omega}_0$ reduce to

$$\Omega_0 \approx \Gamma_{ep}^0(\alpha) b_{ep}(\mu, \alpha)$$

$$\bar{\Omega}_0 \approx \Gamma^0(\alpha) \bar{\beta}_{ep}(\alpha)$$

where $\bar{\beta}_{ep}(\alpha)$ and $b_{ep}(\mu, \alpha)$ are given by Equations IV-(92) and IV-(67) respectively, and $\Gamma_{ep}^o(\alpha)$ is given by

$$\Gamma_{ep}^o(\alpha) = R_{ep} \frac{1}{\alpha^5} J_5^o(\alpha) \quad V-(7)$$

In particular, for $\mu = \left(\frac{\hbar\omega}{KT}\right) \gg \alpha = \left(\frac{\Theta}{T}\right)$, we have

$$b_{ep}(\mu, \alpha) \approx \bar{b}_{ep}(\alpha) = \frac{1}{5J_5^o(\alpha)} \left[J_5^o(\alpha) + \frac{1}{2}\alpha^5 + \alpha^5 \frac{1}{e^{(\alpha)} - 1} \right] \quad V-(8)$$

This relation applies in the spectral range to $\lambda \lesssim 10\mu$.

At very low temperatures ($\alpha \gg 1$), we may use

$$\begin{aligned} \bar{n}_o &\approx \left(\Gamma_{ee}^o(\alpha) + \Gamma_M^o \right) ; \quad T > 0 \\ &\approx \Gamma_M^o ; \quad T \approx 0 \\ n_o &\approx \bar{n}_o \quad \mu \ll \alpha \\ &\approx \left(\frac{R_{ep}}{10} + \Gamma_M^o + \Gamma_{ee}^o \right) \quad \mu \gg \alpha \end{aligned} \quad V-(9)$$

where only Γ_{ee}^o retains a temperature-dependence of $\sim T^2$.

As the numerical computations in a later chapter will show, the residual phonon term $\left(\frac{R_{ep}}{10}\right)$ generally has a value which is comparable with the room temperature value of $(\Gamma_{ep}^o b_{ep})$ and hence is much larger than Γ_M^o and Γ_{ee}^o .

This is clearly in contrast to what might be expected from the classical theory and is also in contrast to the suggestion by Pitaevskii (1958), Silin (1958) and Gurzhi (1959)

that, at low temperatures, only the electron-electron collisions and impurity scattering may play a dominant role. On the other hand, it provides strong support for Holstein's suggestion (Holstein 1954) that the bulk electron-phonon processes may make a large contribution to absorptivity even at a very low temperature.

The quantity, Ω_{ee} , entering in the correction factor $G_{\sigma}(\omega)$ is independent of both frequency and temperature. For convenience in practical applications, we write G_{σ} of Equation (4) into the form

$$G_{\sigma}(\omega) = \left(1 + \frac{R_{ee}}{\Omega_o} \frac{5.29 \times 10^{+6}}{\lambda^2 \theta^2} \right) \quad \text{V-(10)}$$

: λ in μ

It is easily seen that the value of $G_{\sigma}(\omega)$ remains of the order of unity even at very low temperatures, since according to Equation (9),

$$(G_{\sigma}-1) \approx 10 \frac{R_{ee}}{R_{ep}} \frac{5.29 \times 10^{+6}}{\lambda^2 \theta^2} ; \quad \mu \gg \alpha \quad \text{V-(11)}$$

$$\approx \frac{R_{ee}}{\Gamma_M^o} \frac{5.29 \times 10^{+6}}{\lambda^2 \theta^2} ; \quad \begin{array}{l} T \approx 0^\circ K \\ \mu \ll \alpha \end{array}$$

The first equation is not large since $R_{ee} \ll R_{ep}$ and the second is not large since λ^2 is itself large.

In the following part of this chapter, we shall compute various dispersion properties for different spectral ranges applicable at any temperature. Discussion of these properties for different ranges of temperature is omitted since the preceding discussions on the temperature-dependence of Ω_0 , $\tilde{\Omega}_0$, and G_σ are sufficient to specify the temperature-dependence of other dispersion properties.

In what follows, the free-electron spectrum is divided into four segments: [i] $\omega^2 \ll \Omega_0^2, \tilde{\Omega}_0^2 \ll \omega_0^2$; [ii] $\omega^2 \approx \Omega_0^2, \tilde{\Omega}_0^2 \ll \omega_0^2$; [iii] $\Omega_0^2, \tilde{\Omega}_0^2 \ll \omega^2 \ll \omega_0^2$; [iv] $\omega^2 \lesssim \omega_0^2$, where ω_0 is the frequency characteristic of the electron plasma such that $\epsilon > 0$ for $\omega > \omega_0$ and $\epsilon < 0$ (free electron region) for $\omega < \omega_0$.

V-B Optical Constants, n and k

The fundamental relations between the optical constants (n,k) and the dispersion properties (σ, ϵ) were derived from Maxwell's theory of electromagnetic fields in Chapter II. They are:

$$\epsilon(\omega) = (n^2 - k^2)$$

V-(12)

$$\sigma(\omega) = \frac{nk\omega}{2\pi}$$

where (n,k) constitute the real and imaginary parts of the complex index of refraction $\bar{N}(\omega)$;

$$\bar{N}(\omega) = (n - ik)$$

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V-B Optical Constants, n and k

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$$\epsilon(\omega) = (n^2 - k^2)$$

V-(12)

$$\sigma(\omega) = \frac{nk\omega}{2\pi}$$

where (n,k) constitute the real and imaginary parts of the complex index of refraction $\bar{N}(\omega)$;

$$\bar{N}(\omega) = (n - ik)$$

Upon inverting the relations of Equation (12), we obtain (n,k) in terms of (ϵ, σ) as follows;

$$\begin{aligned} n &= \sqrt{\frac{|\epsilon|}{2}} \left[\theta(\omega) + \left\{ 1 + \left(\frac{4\pi\sigma}{\omega\epsilon} \right)^2 \right\}^{\frac{1}{2}} \right]^{\frac{1}{2}} \\ k &= \sqrt{\frac{|\epsilon|}{2}} \left[-\theta(\omega) + \left\{ 1 + \left(\frac{4\pi\sigma}{\omega\epsilon} \right)^2 \right\}^{\frac{1}{2}} \right]^{\frac{1}{2}} \end{aligned} \quad \text{V-(13)}$$

where $\theta(\omega)$ has the meaning,

$$\theta(\omega) = \begin{cases} +1 & \epsilon > 0 \quad (\omega_0 < \omega) \\ -1 & \epsilon < 0 \quad (\omega_0 > \omega) \end{cases}$$

and where ϵ and σ are to be substituted from Equations (1) and (2).

Substitution of Equations (1) and (2) into Equation (13) yields the following expressions of n and k applicable in various spectral ranges where $\omega < \omega_0$;

$$[i] \quad \omega^2 \ll \Omega_0^2, \quad \bar{\Omega}_0^2 \ll \omega_0^2$$

$$\begin{aligned} n \approx k &\approx \frac{1}{\sqrt{2}} \frac{\omega_0}{\sqrt{\omega \Omega_0}} \\ &= \sqrt{\frac{\sigma_{d.c.}}{\nu}} \left[(b_{ep} - 1) \frac{\Gamma_{ep}^0}{\Gamma^0} + 1 \right]^{-\frac{1}{2}} \end{aligned} \quad \text{V-(14)}$$

where

$$\begin{aligned} \sigma_{d.c.} &= \frac{\omega_0^2}{4\pi} \frac{1}{\Gamma^0} = \frac{n_e e^2}{m^*} \frac{1}{\Gamma^0} \\ \Gamma^0 &= \left(\Gamma_{ep}^0 + \Gamma_{ep}^0 + \Gamma_M^0 \right) \end{aligned} \quad \text{V-(15)}$$

At not too low temperatures, we have $\Gamma_{ep}^0 \approx \Gamma^0$, and

$$n \approx k \approx \sqrt{\frac{\sigma_{d.c.}}{\nu}} b_{ep}^{-\frac{1}{2}} \quad V-(16)$$

At very low temperatures,

$$\Gamma^0 \approx \Gamma_{ee}^0 + \Gamma_M^0$$

independent of ω , and

$$\Gamma_{ep}^0 \approx R_{ep} \times 124 \left(\frac{T}{\Theta} \right)^5 \quad V-(17)$$

$$[ii] \quad \omega^2 \approx \Omega_0^2, \tilde{\Omega}_0^2 \ll \omega_0^2$$

$$n \approx \frac{1}{\sqrt{2}} \left(\frac{\omega_0}{\Omega_2} \right) \left[\left\{ 1 + \left(\frac{\Omega_0 \Omega_2}{\omega \Omega_1} G_\sigma \right)^2 \right\}^{\frac{1}{2}} - 1 \right]^{\frac{1}{2}} \quad V-(18)$$

$$k \approx \frac{1}{\sqrt{2}} \left(\frac{\omega_0}{\Omega_2} \right) \left[\left\{ 1 + \left(\frac{\Omega_0 \Omega_2}{\omega \Omega_1} G_\sigma \right)^2 \right\}^{\frac{1}{2}} + 1 \right]^{\frac{1}{2}}$$

$$[iii] \quad \Omega_0, \tilde{\Omega}_0^2 \ll \omega^2 \ll \omega_0^2$$

$$n \approx \frac{1}{2} \frac{\omega_0 \tilde{\Omega}_0}{\omega^2} \tilde{G}_\sigma : \propto (\lambda^2 + \text{constant}) \quad V-(19)$$

$$k \approx \left(\frac{\omega_0}{\omega} \right) : \propto \lambda$$

where $\tilde{\Omega}_0$ and \tilde{G}_σ represent Ω_0 and G_σ with $b_{ep}(\mu, \alpha)$ replaced by $\tilde{b}_{ep}(\alpha)$ given by Equation (8).

$$[iv] \quad \omega^2 \lesssim \omega_0^2$$

$$n \cong \left(\frac{\omega_0^2 - \omega^2}{2\omega_0^2} \right)^{\frac{1}{2}} \left[\left\{ 1 + \left(\frac{\tilde{\Omega}_0 \tilde{G}_\sigma}{\omega} \right)^2 \left(\frac{\omega_0^2}{\omega_0^2 - \omega^2} \right)^2 \right\}^{\frac{1}{2}} - 1 \right]^{\frac{1}{2}}$$

V-(20)

$$k \cong \left(\frac{\omega_0^2 - \omega^2}{2\omega_0^2} \right)^{\frac{1}{2}} \left[\left\{ 1 + \left(\frac{\tilde{\Omega}_0 \tilde{G}_\sigma}{\omega} \right)^2 \left(\frac{\omega_0^2}{\omega_0^2 - \omega^2} \right)^2 \right\}^{\frac{1}{2}} + 1 \right]^{\frac{1}{2}}$$

In particular, when $\omega \approx \omega_0$, we have

$$n \approx k \approx \frac{1}{\sqrt{2}} \left(\frac{\tilde{\Omega}_0 \tilde{G}_\sigma}{\omega_0} \right)^{\frac{1}{2}} \ll 1$$

V-(21)

$$\epsilon \approx 0$$

$$\sigma \approx \frac{\tilde{\Omega}_0}{4\pi}$$

Equations (14) ~ (21), for n and k are plotted qualitatively in Figure 4 as functions of λ .

V-C Absorptivity and Reflectivity

In general, absorption in the free-electron region of the optical spectrum is attributed to two separate mechanisms; bulk process and the anomalous skin effect. The bulk absorption includes contributions by the electron-phonon processes that was suggested by Holstein (1954) and is the heart of the present theory, as well as by the usual electron-electron collisions and impurity scattering. The theory of anomalous skin effects was first offered by Reuter and Sondheimer (1948) and was later elaborated by Dingle (1952, 1953) and Gordon and Sondheimer (1953). Theories which formulate dispersion with consideration of all three, anomalous skin effects, electron-electron collisions and impurity scattering simultaneously, have been developed by Pitaevskii (1958).

Further attempts to formulate the bulk electron-phonon processes have been made and a formula for infrared absorption has been obtained by Gurzhi (1958) by solving the transport equations for conduction electrons.

The infrared absorptivity obtained by Gurzhi applies mostly in the near infrared, and agrees exactly with the result of the present theory in the same limit of the free-electron spectrum, although the calculational methods adopted are different. The present theory applies to virtually the entire free-electron spectrum for all temperatures.

Denoting the bulk absorptivity, skin absorptivity, and total absorptivity as A_B , A_S , and A , respectively, we have

$$A = A_B + A_S \quad V-(22)$$

The total reflectivity R is simply, $(1-A)$. The skin part of absorptivity is important only at very low temperatures, and will be neglected at all other temperatures. The theory of anomalous skin effects was proposed originally in order to explain the low temperature absorption in metals. That skin effects alone cannot explain the observed low temperature absorption has been made clear in a number of papers, and it was to bridge this gap between theory and experiment that Holstein (1954) offered his mechanism of bulk electron-phonon processes. The results of the present theory not only support Holstein's suggestion, but also show that such a bulk mechanism, for many metals, is far more important than the skin absorption even at very low temperatures.

It is well known that, when the anomalous skin effect cannot be neglected, it is diffuse rather than specular reflection of electrons at the metallic surface that contributes to low temperature infrared absorption. Thus, we shall use the well known formula,

$$A_S = \frac{3}{4} \frac{v_F}{c} \quad V-(23)$$

as the absorptivity due to the electrons scattered diffusely

at the surface, where v_F is the Fermi velocity of electrons.

We obtained expressions for the optical constants (n, k) in Equation IV-(13) as functions of the parameters $\epsilon(\omega)$ and $\sigma(\omega)$. Therefore, in order to obtain absorptivity or reflectivity as a function of (ϵ, σ) , we shall make use of the relation,

$$A_B = \frac{4n}{(n+1)^2 + k^2} \quad \text{V-(24)}$$

where (n, k) contain contributions from the bulk alone.

Thus we readily obtain the relation

$$A_B = \frac{2 \left[\theta(\omega) + \left\{ 1 + \left(\frac{4\pi\sigma}{\omega\epsilon} \right)^2 \right\}^{\frac{1}{2}} \right]^{\frac{1}{2}}}{\left[\left[\theta(\omega) + \left\{ 1 + \left(\frac{4\pi\sigma}{\omega\epsilon} \right)^2 \right\}^{\frac{1}{2}} \right]^{\frac{1}{2}} + \sqrt{\frac{|\epsilon|}{2}} \left\{ 1 + \left(\frac{4\pi\sigma}{\omega\epsilon} \right)^2 \right\}^{\frac{1}{2}} + \frac{1}{\sqrt{2|\epsilon|}} \right]} \quad \text{V-(25)}$$

Upon substitution Equations (1) and (2) into the above, we obtain the following results for various spectral ranges with $\omega < \omega_0$;

[i] $\omega^2 \ll \Omega_0^2$, $\bar{\Omega}_0^2 \ll \omega_0^2$ (Generalized Hagen-Rubens formula)

$$\begin{aligned} A_B &\approx 2^{3/2} \left(\frac{\omega \Omega_0}{\omega_0^2} \right)^{\frac{1}{2}} \\ &= 2 \sqrt{\frac{\nu}{\sigma_{d.c.}}} \left(1 + \frac{\Gamma_{ep}^o}{\Gamma_o^o} (b_{ep} - 1) \right)^{\frac{1}{2}} \end{aligned} \quad \text{V-(26)}$$

where the same remarks apply to the correction factor to

the right as in [i] of Section IV-B. This correction factor can be significantly larger than unity at low temperatures. At not too low temperatures, we have $\Gamma_{ep}^0 \approx \Gamma^0$ so that the correction factor is simply $b_{ep}^{\frac{1}{2}}$. Even at room temperature, this can introduce a correction in the order of 10 ~ 20% if

$$\omega^2 > \left(\frac{K\Theta}{\hbar} \right)^2$$

Equation (26) is exactly the Hagen-Rubens formula when the correction factor is equated to unity. The original Hagen-Rubens formula for reflectivity has been found to agree well with observed values, and our formula for reflectivity,

$$R = 1 - 2 \sqrt{\frac{\nu}{\sigma_{d.c.}}} \left(1 + \frac{\Gamma_{ep}^0}{\Gamma^0} (b_{ep} - 1) \right)^{1/2} \quad V-(27)$$

is expected to improve the comparison with the experiment. For this reason, we shall call Equations (26) and (27) the "generalized Hagen-Rubens formula",

$$[ii] \quad \omega^2 \approx \Omega_0^2, \bar{\Omega}_0^2 \ll \omega_0^2 \quad (\lambda \lesssim 10\mu \text{ at } T = 300^\circ K)$$

$$A_B \approx 2^{3/2} \left(\frac{\Omega_2}{\omega_0} \right) \frac{\left[\left\{ 1 + \left(\frac{\Omega_0 \Omega_2}{\omega \Omega_1} G_\sigma \right)^2 \right\}^{1/2} - 1 \right]^{1/2}}{\left[1 + \left(\frac{\Omega_0 \Omega_2}{\omega \Omega_1} G_\sigma \right)^2 \right]^{1/2}} \quad V-(28)$$

$$[iii] \quad \Omega_o^2, \tilde{\Omega}_o^2 \ll \omega^2 \ll \omega_o^2$$

$$A_B \approx 2 \left(\frac{\tilde{\Omega}_o}{\omega_o} \right) \tilde{G}_\sigma(\omega) = \sqrt{\frac{m^*}{\pi n_e e^2}} (\tilde{\Omega}_o \tilde{G}_\sigma) \quad V-(29)$$

where

$$\begin{aligned} (\tilde{\Omega}_o \tilde{G}_\sigma) &= \tilde{\Omega}_o + \frac{\omega^2}{\Omega_{ee}} \\ &= \left(\Gamma_{ep}^o \tilde{b}_{ep} + \Gamma_{ee}^o + \Gamma_M^o + \frac{\omega^2}{\Omega_{ee}} \right) \\ &\approx \left(\Gamma_{ep}^o \tilde{b}_{ep} + \frac{\omega^2}{\Omega_{ee}} \right) : T \gg 0^\circ K \end{aligned} \quad V-(30)$$

At very low temperatures and for $\mu \gg \alpha$, Equation (29) reduces to

$$A_B \approx \sqrt{\frac{m^*}{\pi n_e e^2}} \left(\frac{R_{ep}}{10} + 5.29 \times 10^{+6} \frac{R_{ee}}{\lambda^2 \Theta^2} \right) : \lambda \text{ in } \mu \quad V-(31)$$

The skin term A_s of Equation (23) must be added to obtain the total absorptivity. This formula will be used repeatedly in the future in specific applications, and it will be shown that it gives values in excellent agreement with the experiment. A very interesting feature of Equation (31) is the absence of temperature dependence. Further, the dominant term represented by $\left(\frac{R_{ep}}{10} \right)$ does not contain λ -dependence.

The values of R_{ep} and R_{ee} are in general of the same order of magnitude as Γ_{ep}^0 and Γ_{ee}^0 , respectively, of room temperature so that the quantities within (---) represent a large value while, classically and from some existing quantum mechanical theories, the electron-phonon term is expected to decrease rapidly, like $\sim T^5$, when T is decreased to $0^\circ K$.

Now, let us compare the magnitudes of the two terms with the help of some typical numbers. Many metals have $R_{ep} \approx 10^{13} \sim 10^{15} \text{ sec}^{-1}$ while R_{ee} is of the order of $\sim 10^9 \sim 10^{11} \text{ sec}^{-1}$ and, for an exceptionally large case, $\sim 10^{12} \text{ sec}^{-1}$. Thus, for $R_{ep} = 10^{14} \text{ sec}^{-1}$, $R_{ee} = 10^{10} \text{ sec}^{-1}$, $\theta = 300^\circ K$, and $\lambda = 1\mu$, we have

$$\frac{R_{ep}}{10} = 10^{13} \text{ sec}^{-1}$$

$$5.29 \times 10^6 \frac{R_{ee}}{\lambda^2 \theta^2} \approx (0.06) \times 10^{13} \text{ sec}^{-1}$$

In this case, the electron-electron collisions introduce a correction of about $\sim 6\%$, while, if we take $R_{ee} = 10^{12} \text{ sec}^{-1}$, the correction is as big as 60% . Thus, it is clear that, while the electron-electron collision plays a relatively small part even at very low temperatures for many metals, it can be quite significant for some special cases.

$$[\text{iv}] \quad \omega^2 \lesssim \omega_0^2$$

$$A_B \approx \frac{2 \left[\left\{ 1 + \left(\frac{\tilde{\Omega}_0}{\omega} \tilde{G}_\sigma \right)^2 \left(\frac{\omega_0^2}{\omega_0^2 - \omega^2} \right)^2 \right\}^{\frac{1}{2}} - 1 \right]^{\frac{1}{2}}}{\left[\left[\left\{ 1 + \left(\frac{\tilde{\Omega}_0}{\omega} \tilde{G}_\sigma \right)^2 \left(\frac{\omega_0^2}{\omega_0^2 - \omega^2} \right)^2 \right\}^{\frac{1}{2}} - 1 \right]^{\frac{1}{2}} + \left(\frac{\omega_0^2 - \omega^2}{2\omega^2} \right)^{\frac{1}{2}} \left[1 + \left(\frac{\tilde{\Omega}_0}{\omega} \tilde{G}_\sigma \right)^2 \left(\frac{\omega_0^2}{\omega_0^2 - \omega^2} \right)^2 \right]^{\frac{1}{2}} + \left(\frac{\frac{1}{2}\omega^2}{\omega_0^2 - \omega^2} \right)^{\frac{1}{2}} \right]} \quad \text{V-(31)}$$

In particular, at $\omega^2 \approx \omega_0^2$, this is reduced to

$$A_B \approx 2^{3/2} \left(\frac{\tilde{\Omega}_0 \tilde{G}(\omega_0)}{\omega_0} \right)^{\frac{1}{2}} \quad \text{V-(32)}$$

At such large frequencies, the second term in $G_\sigma(\omega)$ due to electron-electron collisions may become predominant, especially for those metals which have large values of R_{ee} .

The bulk absorptivity and reflectivity are plotted qualitatively in Figure 5, where the significance of the correction factor $G_\sigma(\omega)$ is shown in the high-frequency limit.

V-D Temperature-Dependent Scattering Cross-Section, Optical Size of Electrons, and the Virtual Mass of Light Quantum

From our formulae for temperature-dependent optical constants (n, k) or (σ, ϵ) , we can define the temperature-dependent scattering amplitude, scattering cross-section per electron, and hence the optical radius of the electron. By scattering cross-section we mean the effective cross-section of a conduction electron which the external electromagnetic field sees for interaction, including both pure scattering and absorption. In this sense, it may also be called "the dispersion cross-section per electron". If such a cross-section is denoted as $\sigma_s(\omega, T)$ measured in cm^2 , the optical radius of an electron, a_s , is defined as

$$\pi a_s^2 = \sigma_s \quad \text{V-(33)}$$

and is measured in cm.

The concept of "virtual mass of a photon" in metals (and also in dielectric media as well) is a rather new one and its definition is helpful in a qualitative discussion of infrared dispersion in metals. A light quantum of frequency ω , when it enters a medium with index of refraction $n > 1$, behaves as a light quantum of frequency, $\left(\frac{\omega}{n}\right) < \omega$, as if it suddenly gained a nonzero mass m_p and that

$$\omega^2 = \left(\frac{\omega}{n} \right)^2 + K_p^2 c^2 \quad \text{V-(34)}$$

$$K_p = \left(\frac{m_p c}{\hbar} \right)$$

This is a relation which is often used to obtain the expression of n in dielectric crystals, and is not anything particularly new. A quick glance at the relation reminds us of the familiar expression for relativistic energy of a particle in terms of kinetic and mass terms. Thus, we may conveniently define the first term of Equation (34) as the kinetic term and the second as the mass term, so that

$$m_p = \frac{\hbar \omega}{c^2} \frac{\sqrt{n^2 - 1}}{n} \geq 0 \quad \text{V-(35)}$$

Likewise, we may treat the mass term as a potential term such that an increase in m_p and hence a decrease in the kinetic term correspond to an increase in a potential of some kind. In fact, the physical picture of some dispersion properties, at least in the free-electron region, can be better understood in terms of such an argument. For instance, the increase of reflectivity of light by a metal with increase in index of reflection may be explained in analogy with the increase in backward scattering of a particle by an increased positive potential step, and hence a smaller kinetic energy in the new potential field. We are essentially applying our knowledge of the elementary particle picture to optical

dispersion in contrast to the usual practice of applying optics to massed particles.

We shall now calculate various properties explained above with the help of the relations of Chapter II. Upon combining Equations (1) and (2) with the dispersion relations for n and k of Chapter II, we easily obtain the following temperature-dependent expressions for the real and imaginary parts of the scattering amplitudes, $(R_e \bar{F})$ and $(I_m \bar{F})$;

$$\begin{aligned} R_e \bar{F} &= r_o^* \left(\frac{\omega}{\omega_o} \right)^2 \sqrt{2|\epsilon|} \left[\left\{ -1 + \left[1 + \left(\frac{4\pi\sigma}{\omega\epsilon} \right)^2 \right]^{\frac{1}{2}} \right\}^{\frac{1}{2}} - \sqrt{\frac{2}{|\epsilon|}} \right] \\ I_m \bar{F} &= r_o^* \left(\frac{\omega}{\omega_o} \right)^2 \sqrt{2|\epsilon|} \left[1 + \left\{ 1 + \left(\frac{4\pi\sigma}{\omega\epsilon} \right)^2 \right\}^{\frac{1}{2}} \right]^{\frac{1}{2}} \end{aligned} \quad V-(36)$$

where r_o^* is the effective classical radius of electrons and is related to the usual classical radius of electron r_o as

$$r_o^* = \frac{e^2}{m^* c^2} = \left(\frac{m_o}{m^*} \right) r_o \quad V-(37)$$

where m_o is the rest mass of an electron.

The scattering cross-section σ_s and the optical radius a_s are obtained from the usual relation,

$$\sigma_s = \pi a_s^2 = \frac{4\pi c}{\omega} I_m \bar{F} \quad V-(38)$$

The mass of a photon m_p is computed from Equation (35) by using the formulae for $n(\omega)$ that were obtained in Chapter IV-B. Here again, we shall compute these quantities for various segments of the free-electron spectrum when $\omega < \omega_0$. They are:

$$[1] \quad \omega^2 \ll \Omega_0^2, \quad \bar{\Omega}_0^2 \ll \omega_0^2;$$

$$R_e \bar{F} \approx I_m \bar{F} \approx \sqrt{2} \quad r_0^* \left(\frac{\omega^3}{\omega_0^2 \Omega_0} \right)^{\frac{1}{2}}$$

$$\sigma_s \approx 4\pi \sqrt{2} \quad c \quad r_0^* \left(\frac{\omega}{\omega_0^2 \Omega_0} \right)^{\frac{1}{2}} \quad V-(39)$$

$$a_s \approx 2^{\frac{3}{4}} \left(\frac{r_0^* \lambda_0}{\pi} \right)^{\frac{1}{2}} \left(\frac{\omega}{\Omega_0} \right)^{\frac{1}{4}} \quad V-(40)$$

$$m_p \approx \frac{\hbar \omega}{c^2} \quad V-(41)$$

where λ_0 is the critical wavelength

$$\lambda_0 = \frac{2\pi c}{\omega_0}$$

We notice that $m_p c^2$ is nearly the entire photon energy $\hbar \omega$ meaning that, in this part of the spectrum, the photon may seem nearly motionless to a Fermi electron of speed

$v_F \approx 10^8$ (cm/sec), and hence there is a greater probability of encounter, on the average, between the photon of mass m_p and the conduction electrons during the period of $\left(\frac{2\pi}{\omega} \right)$ (second).

$$[ii] \quad \omega^2 \approx \Omega_0^2, \tilde{\Omega}_0^2 \ll \omega_0^2$$

$$R_{e\bar{F}} \approx \sqrt{2} r_0^* \frac{\omega^2}{\omega_0 \Omega_2} \left[\left\{ 1 + \left(\frac{\Omega_0 \Omega_2}{\omega \Omega_1} G_\sigma \right)^2 \right\}^{\frac{1}{2}} - 1 \right]^{\frac{1}{2}} \quad V-(42)$$

$$I_{m\bar{F}} \approx \sqrt{2} r_0^* \frac{\omega^2}{\omega_0 \Omega_2} \left[\left\{ 1 + \left(\frac{\Omega_0 \Omega_2}{\omega \Omega_1} G_\sigma \right)^2 \right\}^{\frac{1}{2}} + 1 \right]^{\frac{1}{2}} \quad V-(43)$$

$$\sigma_s \approx 2 \sqrt{2} r_0^* \lambda_0 \left(\frac{\omega}{\Omega_2} \right) \left[1 + \left\{ 1 + \left(\frac{\Omega_0 \Omega_2}{\omega \Omega_1} G_\sigma \right)^2 \right\}^{\frac{1}{2}} \right]^{\frac{1}{2}} \quad V-(44)$$

$$a_s \approx 2^{\frac{3}{4}} \left(\frac{\lambda_0 r_0^*}{\pi} \right)^{\frac{1}{2}} \left(\frac{\omega}{\Omega_2} \right)^{\frac{1}{2}} \left[1 + \left\{ 1 + \left(\frac{\Omega_0 \Omega_2}{\omega \Omega_1} G_\sigma \right)^2 \right\}^{\frac{1}{2}} \right]^{\frac{1}{2}} \quad V-(45)$$

$$m_p \approx \frac{\hbar \omega}{c^2}$$

$$[iii] \quad \Omega_0^2, \tilde{\Omega}_0^2 \ll \omega^2 \ll \omega_0^2$$

$$R_{e\bar{F}} \approx 2 r_0^* \left(\frac{\omega}{\omega_0} \right)^2 \left[\frac{1}{2} \frac{\omega_0 \tilde{\Omega}_0}{\omega^2} \tilde{G}_\sigma - 1 \right] \quad V-(46)$$

$$I_{m\bar{F}} \approx 2 r_0^* \left(\frac{\omega}{\omega_0} \right) \quad V-(47)$$

$$\sigma_s \approx 4 r_0^* \lambda_0 \quad V-(48)$$

$$a_s \approx \frac{2}{\sqrt{\pi}} (r_o^* \lambda_o)^{\frac{1}{2}} \quad V-(49)$$

$$m_p \approx \frac{\hbar \omega}{c^2} \left[1 - 4 \left(\frac{\omega^2}{\omega_o^2 \tilde{\gamma}_o \tilde{\gamma}_\sigma} \right)^2 \right]^{\frac{1}{2}} \quad V-(50)$$

It is seen that σ_s and a_s are independent of frequency and temperature while we found previously that absorptivity is independent of frequency in this part of the spectrum. Formula (50) for m_p necessitates defining a frequency ω_m such that $m_p = 0$ at $\omega = \omega_m$ given by

$$\omega_m^2 = \frac{\tilde{\gamma}_o \omega_o}{2 - \frac{\omega_o}{\tilde{\gamma}_{ee}}} > 0 \quad V-(51)$$

Strictly speaking, relation (50) is valid only for ω smaller than ω_m . This corresponds to the point where the index of refraction is identically equal to unity and the light quantum behaves as though the bulk of the metal is not different from vacuum. Photoelectric processes which may be important at such a frequency have been neglected.

$$[iv] \quad \omega^2 \lesssim \omega_o^2$$

$$R_e \bar{F} \approx 2r_o^* \left(\frac{\omega}{\omega_o} \right)^2 \left\{ \left(\frac{\omega_o^2 - \omega^2}{2\omega_o^2} \right)^{\frac{1}{2}} \left[1 + \left\{ 1 + \left(\frac{\tilde{\gamma}_o}{\omega} \right)^2 \left(\frac{\omega_o^2 \tilde{\gamma}_\sigma}{\omega_o^2 - \omega^2} \right)^2 \right\}^{\frac{1}{2}} \right]^{\frac{1}{2}} - 1 \right\} \quad V-(52)$$

$$I_m \bar{F} \approx 2r_o^* \left(\frac{\omega}{\omega_o} \right)^2 \left(\frac{\omega_o^2 - \omega^2}{2\omega_o^2} \right)^{\frac{1}{2}} \left[\left\{ 1 + \left(\frac{\tilde{\gamma}_o}{\omega} \right)^2 \left(\frac{\omega_o^2 \tilde{\gamma}_\sigma}{\omega_o^2 - \omega^2} \right)^2 \right\}^{\frac{1}{2}} + 1 \right]^{\frac{1}{2}} \quad V-(53)$$

$$\sigma_s \approx 2^{3/2} (r_o^* \lambda_o) \left(1 + \frac{1}{2} \frac{\Delta\omega}{\omega_o}\right) \left(\frac{\tilde{n}_o}{\omega_o} \tilde{G}_\sigma\right)^{\frac{1}{2}} \quad V-(54)$$

$$a_s \approx 2^{3/4} \left(\frac{r_o^* \lambda_o}{\pi}\right)^{\frac{1}{2}} \left(1 + \frac{1}{2} \frac{\Delta\omega}{\omega_o}\right) \left(\frac{\tilde{n}_o}{\omega_o} \tilde{G}_\sigma\right)^{\frac{1}{2}} \quad V-(55)$$

where $\Delta\omega = (\omega - \omega_o)$.

When $\omega \gg \omega_o$, both σ_s and a_s approach very small but constant values of the order, $\left(\frac{\tilde{n}_o}{n_{ee}}\right)$ and $\left(\frac{\tilde{n}_o}{n_{ee}}\right)^{\frac{1}{2}}$, respectively, and vanish identically when there is no Umklapp process present. This is, of course, not strictly true when we consider the contribution of bound electrons which are important in this part of the spectrum.

The scattering cross-section σ_s is plotted against λ qualitatively in Figure 6. The λ -dependence of m_p is also shown. The general pattern in the λ -dependence of σ_s and $\left(\frac{m_c c^2}{\hbar \omega}\right)$ may be compared with those of absorptivity and reflectivity, respectively, of Figure 5.

Chapter VI

Paramagnetic and Ferromagnetic Transition Metals

VI-A Introduction

The calculation presented in the preceding chapters depend on the assumption that the energy surface is spherical. This assumption has been shown to work well for a variety of nontransition metals. However, for many multivalent and transition metals which have been investigated from a theoretical point of view, the surface of the Fermi level cuts through two or more Brillouin zones, and it does not resemble the spherical shape we considered in Chapters IV and V.

In particular, the study of ferromagnetic and paramagnetic transition elements represents a special problem from a theoretical point of view, since the metallic properties of these metals have a rather peculiar dependence on the place of the element in the periodic table. These special properties are exhibited in the observed temperature dependences of resistivity as well as of various thermodynamic properties. Behavior of the ferromagnetic transition metals represents an even more special case. Although these metals have been studied rather extensively as to their d.c. electrical properties based on the quantum mechanical explanations, very little work has been done on the optical and infrared dispersion

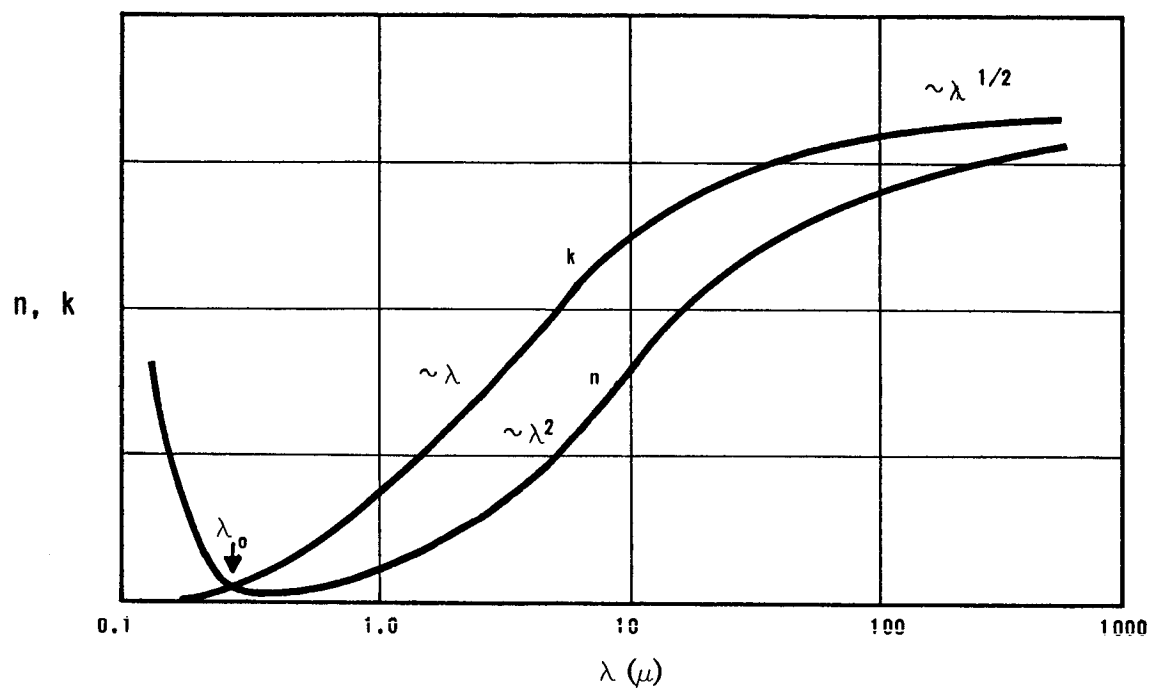


FIGURE 4

Typical Curves of the Optical
Constants n and k vs λ

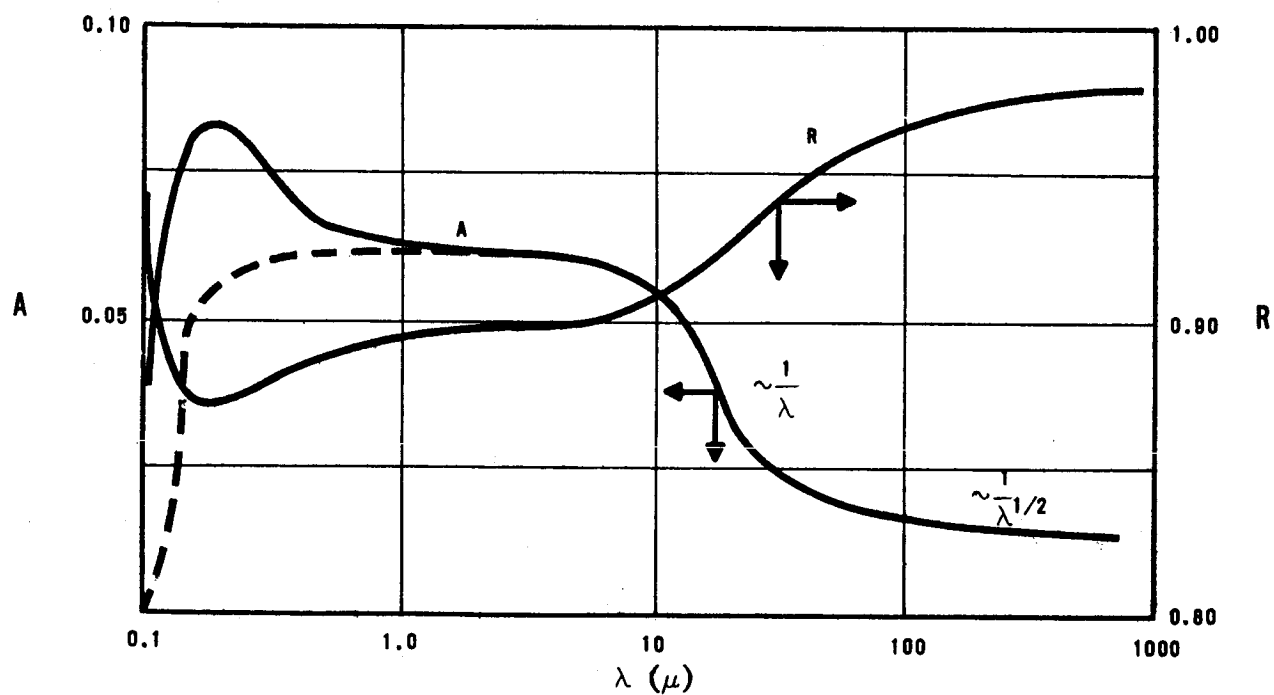


FIGURE 5

Typical Curve of Absorptivity as a
Function of Wavelength

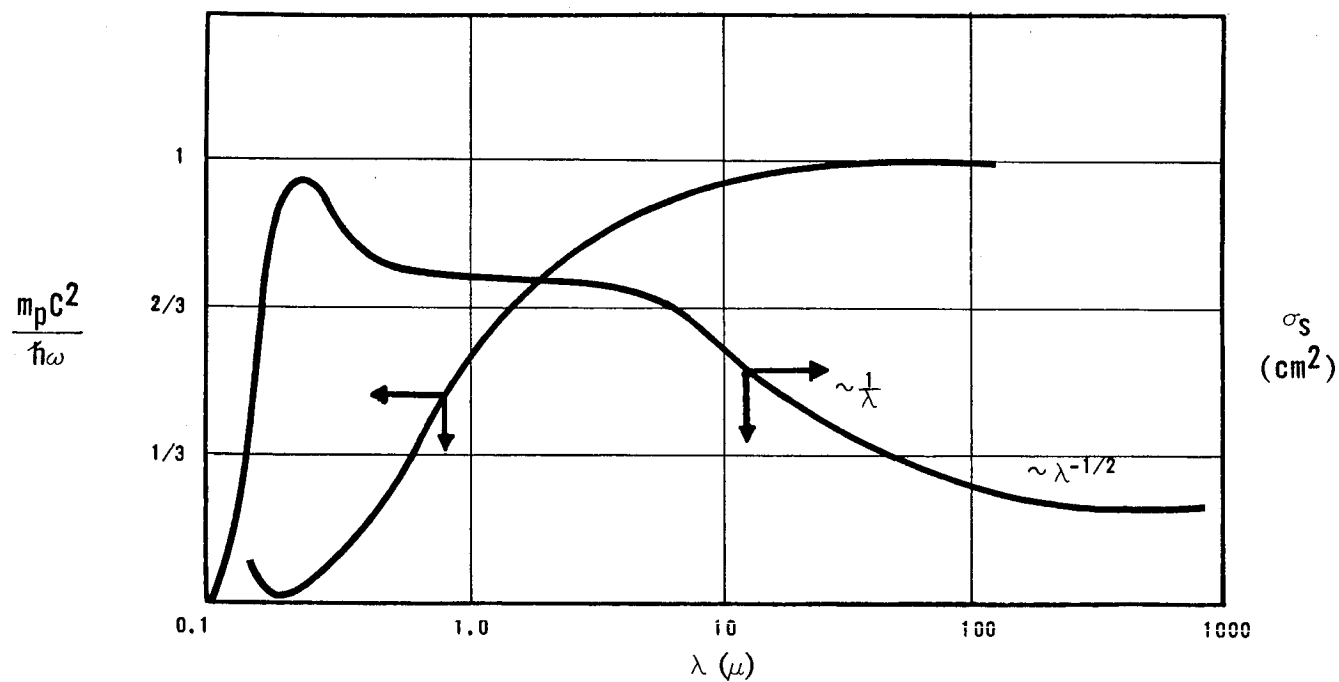


FIGURE 6

Typical λ - Dependence of the Scattering Cross-Section σ_s per Conduction Electron and of the Photon Mass m_p

properties. Some of the qualitative features of the optical properties of transition metals and transition metal alloys were presented by Mott (1936, 1935).

In the transition metals such as Pt, Pd, Ir and Ni, the s-band and d-band overlap and the Fermi level falls in this overlapping region. The most widely investigated metals are the triad, Pt, Pd and Ni, which come before Cu, Ag and Au in the periodic table, and are all face-centered cubic lattices. In palladium, there is about 0.55-0.6 electron per atom in 5s states and the same number of holes in the 4d states. In pure platinum, there is about 0.55-0.6 electron in 6s states and the same number of holes in 5d states. In nickel, there is about 0.55-0.6 electron in 4s states and the same number of holes in 3d states. The density of states $\rho(E)$ of 4s and 3d states of nickel is schematically illustrated in Figure 33 and are compared with 4s and 3d states of copper. The large value of energy density of d states compared with s states is qualitatively indicated, and it will be shown that this leads to important consequences.

Some of the important physical consequences of the presence of positive holes in the d-band are: (a) the ferromagnetism or high paramagnetism shown by these metals; (b) the low electrical conductivity and anomalous behavior of resistance both at high and low temperatures; (c) the low reflection coefficient for long wavelengths; and

(d) the high electronic specific heat. Although all the above properties are mutually related, only the first three will enter explicitly in calculations of optical and infrared dispersion properties. In the language of the optical dispersion theory, the low reflectivity for long wavelengths is the direct consequence of the low electrical conductivity. This may be explained on the basis of the Hagen-Rubens formula for reflectivity R that is applicable at long wavelengths,

$$R \approx 1 - 2 \sqrt{\frac{\omega}{2\pi\sigma_{dc}}}$$

where it is seen that a low value of $\sigma_{d.c.}$, the d.c. conductivity, results in a low value of reflectivity.

The low electrical conductivity is a direct consequence of the large density of states in the d-band. The transition matrix elements that contribute to resistivity or the inverse of the relaxation time τ_R contains a predominantly large contribution from the $s \rightarrow d$ transitions, since the probability of such a transition is multiplied by the large value of the density of states of the final d states. In fact, the interband transitions from s to d states alone account for 90% or more of the conductivity because of the large value of the transition probability compared with the other modes of transitions, $s \rightarrow s$, $d \rightarrow s$, $d \rightarrow d$.

For the particular case of the ferromagnetic nickel, three states of electronic configuration are possible: namely, $3d^8 4s^2$, $3d^9 4s^1$, and $3d^{10}$ states. The wave function for each atom will be a superposition of the atomic wavefunctions corresponding to different electronic configurations. If ψ_2 , ψ_1 and ψ_0 are the wavefunctions corresponding to the three configuration states in the order listed above, the wavefunction in an atom of the solid nickel will be in the form,

$$A_2\psi_2 + A_1\psi_1 + A_0\psi_0$$

where $|A_2|^2$, $|A_1|^2$, and $|A_0|^2$ are constants representing the fraction of occurrence of each of the three configurations. The mean number of electrons in the s states is then given by

$$\bar{n}_s = 2 \times |A_2|^2 + 1 \times |A_1|^2 \quad \text{VI-(1)}$$

which is equal to $0.55 \sim 0.6$ per atom. This is also equal to the number of positive holes in the d-band. Another consideration enters in the study of nickel on account of the ferromagnetic properties. It is outside the scope of the present work to discuss in detail the mechanism that gives rise to the ferromagnetism. We are only interested in the way the ferromagnetism enters in the optical and infrared dispersion of metal. It is sufficient to note that,

in the ferromagnetic nickel, the d states with one orientation of the electron spin are filled, and the holes occur only for those states of the d-band which correspond to the electron spins oriented antiparallel to these filled states. The electrons in the s states, however, occur in equal mixture of the two spin states. The result of this is that there is a residual spin component equal to the mean number of positive holes times the electron spin. Since the mean number of holes per atom is exactly equal to the mean number of s electrons, the residual spin per nickel atom at 0°K is

$$\frac{\hbar}{2} \bar{n}_s = (0.55 \sim 0.60) \frac{\hbar}{2}$$

The residual spin or the spontaneous magnetization decreases gradually as temperature is increased, and the metal turns paramagnetic as temperature is increased further beyond the Curie point.

The important consequence of this property that will be of concern in our calculations is that not all of the s-electrons are qualified to make transitions to the empty d states: only those s-electrons with the spins antiparallel to the residual spin of the d states will be able to make transitions because of the Pauli exclusion principle. At 0°K, only $\frac{1}{2}$ of the s-electrons are qualified, while, at a temperature above the Curie point, practically all of the

s-electrons are qualified. This explains the large increase in the observed resistivity of Ni above the Curie point (Gerlach, 1932), since the damping contributed by the transitions is directly proportional to the number of d states which are available for the transitions.

In short, the electrical properties and hence the optical and infrared behavior of a ferromagnetic metal will be a function of both the spontaneous magnetization Σ and temperature.

If we denote the spontaneous magnetization per gram atom at any temperature $T^\circ\text{K}$ and at 0°K by $\Sigma(T)$ and Σ_0 , respectively, the total number of s-electrons that are qualified to make transitions to the empty d states may be defined as

$$\bar{n}_s = \frac{n_s}{2} \chi = \frac{n_s}{2} \left[1 + \frac{\Sigma_0 - \Sigma}{\Sigma_0} \right] \quad \text{VI-(2)}$$

$$: 1 \leq \chi \leq 2$$

where n_s is the effective number of electrons in the s-band. This shows immediately that resistivity of nickel has an additional temperature dependence coming from Σ besides the usual temperature dependence coming from the lattice vibrations. The explicit temperature dependence of the

factor χ is available from the phenomenological theory of Weiss (1907) at high temperature and the quantum mechanical theory of Heisenberg (1926) at low temperatures. A detailed theoretical and phenomenological discussion on ferromagnetism and paramagnetism is offered by Van Vleck (1959). For the purpose of our calculation that will follow, it is sufficient to note that the phenomenological theory of Weiss shows that $(\chi-1)$ increases with increasing T like

$$e^{-\text{constant}/T}$$

at high temperatures (viz., $T > 400^\circ\text{K}$), and that the theory of Heisenberg shows that $(\chi-1)$ decreases like $T^{3/2}$ at low temperatures as T is decreased. The observed and theoretical values of χ and Σ are shown in Table VIII at different temperatures for the ferromagnetic metals, Ni, Co, Fe and others.

In the following part of the present chapter, probability of the $s \rightarrow d$ transitions will be calculated by a method similar to what was adopted in Chapter IV for the intraband transitions. All the other modes of transitions, $d \rightarrow d$, $s \rightarrow s$, and $d \rightarrow s$ will be neglected compared with the $s \rightarrow d$ transitions.

The weight factor multiplying the $s \rightarrow d$ transition probability is about 10 times the normal scattering probability according to the evidence provided by the data on the electronic specific heat (Wilson, 1936). This means that

neglecting all modes of transitions other than the s-band to d-band transition will introduce an error of about 10% in the calculated resistivity. Besides, the results on the intraband transitions are satisfactorily presented by the calculations of Chapter IV.

Finally, it may be noted that the results that are obtained in the present chapter should be applicable just as well to interband transitions in other multivalent metals. For nontransition multivalent metals, the interband transitions do not necessarily contribute more than the intraband transitions. Whatever the case may be, it is useful to remember that the total damping coefficient, including both the interband and intraband transitions, can be obtained simply by adding the damping coefficient that is obtained in the present chapter to that obtained in Chapter IV for intraband transitions.

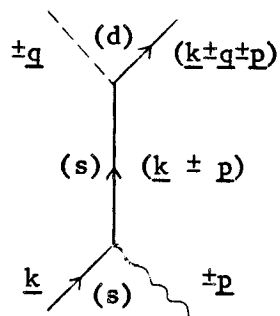
VI-B Calculation of Transition Probability

Because of the large effective mass of the d-electrons, their contribution to conductivity will be small and can be neglected compared with that due to the s-electrons. The empty states in the d-band have a considerable effect in that the s-electrons can be scattered not only into energy levels in the s-band but also into the d-band. The large value of the density of states in the final d states makes

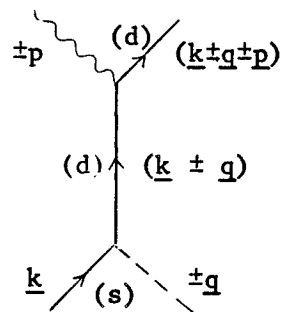
the $s \rightarrow d$ transition probability much larger than the normal $s \rightarrow s$ transition probability. Further, the $d \rightarrow d$ and $d \rightarrow s$ transition probabilities together are even smaller than the $s \rightarrow s$ transition probability due to large values of the effective mass m_d of d-electrons compared with that of s-electrons, m_s .

For this reason, the following calculations will include only the $s \rightarrow d$ transitions. Contribution to the conductivity coming from the $s \rightarrow d$ transitions alone explains at least 90% of the total conductivity according to the evidence obtained from the data on the electronic specific heat (Wilson, 1936), 1938). In order to obtain the contributions of the $s \rightarrow s$ transition, results of Chapter IV may be used without necessity of modification. Calculations of the $s \rightarrow d$ transition probability involve essentially the same theoretical approach as that adopted in Chapter IV. The $s \rightarrow d$ transition caused by a joint action of both the electromagnetic field and the phonon field is again a second-order effect, and may be calculated from the second-order coefficient $B_{(2)}^{s \rightarrow d}(\underline{k})$ representing such a transition. There are eight different processes for the $s \rightarrow d$ transitions, four of which involve creation or annihilation of a photon in the s-band, while the other four involve creation or annihilation of a photon in the d-band. These eight processes are illustrated schematically in the accompanying Feynmann

diagrams where (A) shows the first four processes and (B) shows the other four processes.



(A)



(B)

In the diagrams, the solid, curved, and broken lines represent the electron, photon, and phonon, respectively.

The coefficient $B_{(2)}^{s \rightarrow d}(\underline{k} \pm \underline{q} \pm \underline{p})$ may be calculated by essentially the same method as that adopted in Chapter IV. We thus obtain the following two equations corresponding to (A) and (B);

$$B_{(2)}^{s \rightarrow d}(\underline{k} \pm \underline{q} \pm \underline{p}) \Big|_{(A)} = \mp |\underline{q}| \left(\frac{\hbar^2}{2N_p M V E_q} \right)^{\frac{1}{2}} \left(\frac{\sqrt{N_q}}{\sqrt{1+N_q}} \right) \frac{e \hbar g^{sd}}{m_s \omega} (\underline{E} \cdot \underline{k})$$

VI-(3)

$$\times \frac{(-1)}{E(\underline{k} \pm \underline{p}) - E(\underline{k}) \mp \hbar \omega} \left[\frac{1 - e^{i \xi t / \hbar}}{\xi} - \frac{1 - e^{i \xi' t / \hbar}}{\xi'} \right]$$

$$\begin{aligned}
 B_{(2)}^{s \rightarrow d}(\underline{k} \pm \underline{q} \pm \underline{p}) \Big|_{(B)} &= \pm |\underline{q}| \left(\frac{\hbar^2}{2N_p M V E_{\underline{q}}} \right)^{\frac{1}{2}} \left(\frac{\sqrt{N_q}}{\sqrt{1+N_q}} \right) \frac{e \hbar g^{sd}}{m_d \omega} \underline{E} \cdot (\underline{k} \pm \underline{q}) \\
 &\times \frac{(-1)}{E'(\underline{k} \pm \underline{q}) - E(\underline{k}) \mp E_{\underline{q}}} \left[\frac{1 - e^{i\xi t/\hbar}}{\xi} - \frac{1 - e^{i\xi'' t/\hbar}}{\xi''} \right] \quad \text{VI-(4)}
 \end{aligned}$$

where the energy terms denoted as ξ , ξ' , and ξ'' in various resonance factors are given by

$$\begin{aligned}
 \xi &= \left\{ E'(\underline{k} \pm \underline{q} \pm \underline{p}) - E(\underline{k}) \mp \hbar \omega \mp E_{\underline{q}} \right\} \\
 \xi' &= \left\{ E'(\underline{k} \pm \underline{q} \pm \underline{p}) - E(\underline{k} \pm \underline{p}) \mp E_{\underline{q}} \right\} \\
 \xi'' &= \left\{ E'(\underline{k} \pm \underline{q} \pm \underline{p}) - E'(\underline{k} \pm \underline{q}) \mp \hbar \omega \right\}
 \end{aligned} \quad \text{VI-(5)}$$

The energy $E'(\underline{k})$, with a prime, represents the energy of a d-electron and $E(\underline{k})$, without a prime, represents the energy of a s-electron with momentum ($\hbar \underline{k}$):

$$\begin{aligned}
 E'(\underline{k}) &= E_0 - \frac{\hbar^2}{2m_d} k^2 \\
 E(\underline{k}) &= \frac{\hbar^2 k^2}{2m_s}
 \end{aligned} \quad \text{VI-(6)}$$

where E_0 is the energy at the upper edge of the d-band. The constant factor g^{sd} represents the strength of the electron-phonon interaction which is generally of the same

order of magnitude as the energy of an electron and has the same meaning as g which was used in Chapter IV. As usual taking g^{sd} and also g to be independent of the energy of the electron which is interacting with a phonon is the result of assuming that the electron-ion potential within single unit-cell is reasonably flat, or equivalently that the radius of the atomic core is much smaller than the size of a single unit-cell. This assumption is satisfactory for common applications such as in the present theory. The more general electron-phonon interaction which also includes the deformation of ions was discussed by Bardeen (1937). A further discussion on this problem is offered in the 1958 edition of The Theory of Metals by Wilson.

As in Chapter IV, we shall ignore the quantities of the order of $\left(\frac{v_F}{c}\right)$, and take

$$E(\underline{k} \pm \underline{p}) - E(\underline{k}) \mp \hbar\omega \approx$$

$$E'(\underline{k} \pm \underline{q} \pm \underline{p}) - E'(\underline{k} \pm \underline{q}) \mp \hbar\omega \approx \mp \hbar\omega$$

VI-(7)

Then, of all the terms in Equations (3) and (4), only those which have ξ in the resonance factors need be considered for our calculations, since the others will contribute equally to both the emission and absorption of a photon and will thus cancel out when we calculate the net absorption by subtracting the emission term from the absorption term.

By combining Equations (3) and (4), and using the relation

$$\left[\frac{\underline{k}}{E(\underline{k} \pm \underline{p}) - E(\underline{k}) \mp \hbar\omega} - \frac{m_s}{m_d} \frac{(k \pm q)}{E'(\underline{k} \pm \underline{q}) - E(\underline{k}) \mp E_q} \right]_{\xi=0} \cong \frac{\underline{k} \left(1 + \frac{m_s}{m_d} \right) \pm \frac{m_s}{m_d} q}{\mp \hbar\omega} \quad \text{VI-(8)}$$

we now have

$$B_{(2)}^{s \rightarrow d}(\underline{k} \pm \underline{q} \pm \underline{p}) \cong \pm |q| \left(\frac{\hbar^2}{2N_p M V E_q} \right)^{\frac{1}{2}} \left(\frac{\sqrt{N_q}}{\sqrt{1+N_q}} \right) \frac{e g^{sd}}{\mp m_s \omega^2} \quad \text{VI-(9)}$$

$$\times E_0 \left\{ \underline{k} \left(1 + \frac{m_s}{m_d} \right) \pm \frac{m_s}{m_d} q \right\} \frac{1 - e^{i\xi t/\hbar}}{\xi}$$

It may be noted that the value $\left(\frac{m_s}{m_d} \right)$ of a transition metal is usually very much smaller than unity $\left(\approx \frac{1}{10} \right)$ and such a term in Equation (9) can be neglected without any loss in the qualitative merit of our calculations. It is retained in Equation (9), however, because this term can be important when the results are applied to non-transition multivalent metals for which the ratio of the effective mass values is not necessarily small.

The probability for the process in which an electron in the s-band with momentum \underline{k}_1 makes a transition to

the d-state with momentum \underline{k}_2 by a joint action of the electromagnetic and phonon fields is obtained from Equation (9) upon using the usual relation,

$$P_{(s)}^{(r)}(\underline{k}_1 \rightarrow \underline{k}_2) = \lim_{T \rightarrow \infty} \left| B_{(2)}^{s \rightarrow d}(\underline{k}_1 \rightarrow \underline{k}_2) \right|^2 / T \quad \text{VI-(10)}$$

where we have put $\underline{k} \rightarrow \underline{k}_1$ and $\underline{k}_2 = (\underline{k}_1 \pm \underline{q} \pm \underline{p})$, and $r = (\pm)$, $s = (\pm)$ correspond to emission and absorptions of phonons and photons, respectively. Thus, we obtain

$$P_{(s)}^{(r)}(\underline{k}_1 \rightarrow \underline{k}_2)_{s \rightarrow d} = \frac{e^2 \hbar^4 E^2}{12 V m_s^2 (\hbar \omega)^4} G_{sd}^{(r)}(\underline{q}) \quad \text{VI-(11)}$$

$$\times (q^2 \left(\frac{m_s}{m_d} \right)^2 + k_1^2 \left(1 + \frac{m_s}{m_d} \right)^2) \delta(E_2' - E_1 + r E_{\underline{q}} + s \hbar \omega)$$

$$: E_2' = E'(\underline{k}_2) = E_0 - \frac{\hbar^2}{2m_d} (k_2)^2$$

where we have taken

$$\overline{(\underline{E} \cdot \underline{k}_1)(\underline{E} \cdot \underline{q})} = 0$$

$$\frac{\overline{(\underline{E} \cdot \underline{k}_1)^2}}{k^2} = \frac{\overline{(\underline{E} \cdot \underline{q})^2}}{q^2} = \frac{1}{3} E^2$$

and

$$G_{sd}^{(r)}(\underline{q}) = \frac{\pi \hbar q^2 g_{sd}^2}{N_p M E_{\underline{q}}} \begin{pmatrix} 1 + N_q \\ N_q \end{pmatrix} \quad \text{VI-(12)}$$

The probability for an electron initially at the state of energy E_1 in the s-band to make a transition to the final state of energy E_2' in the d-band is defined as

$$P_{(s)}^{(r)}(E_1)_{sd} = 2 \sum_{\underline{k}_2} P_{(s)}^{(r)}(\underline{k}_1 \rightarrow \underline{k}_2) [1 - F(E_2')] \quad \text{VI-(13)}$$

where the factor 2 is multiplied because two electrons with opposite spins can occupy the state of same momentum \underline{k}_2 according to the Pauli exclusion principle, and $F(E_2')$ is the Fermi function evaluated at the final state E_2' .

The summation over \underline{k}_2 may be replaced by the summation over the phonon momentum \underline{q} and hence by an integral

$$\frac{V}{(2\pi)^3} \iiint (d\underline{q}) \dots\dots$$

provided that we are careful in establishing the integral limits in the integral over \underline{q} since the density of states at the final state now contain a factor

$$\sqrt{E_0 - E_2}$$

instead of \sqrt{E} . Occurrence of the factor $\sqrt{E_0 - E}$ instead of \sqrt{E} in the density-of-states function leads to the lower limit in the q -integral given by

$$q_{\min} = |k_d - k_s| \quad \text{VI-(14)}$$

where k_d and k_s are the momenta corresponding to the highest occupied levels in the d - and s -bands, respectively, and are given by those at the Fermi level according to the relations,

$$\begin{aligned} k_s &= \left(\frac{2m_s}{\hbar^2} E_F \right)^{\frac{1}{2}} \\ k_d &= \left[\frac{2m_d}{\hbar^2} (E_0 - E_F) \right]^{\frac{1}{2}} \end{aligned} \quad \text{VI-(15)}$$

Equation (13) is solved by removing the delta function through integration over the angular variable $\cos \theta = \left(\frac{\mathbf{k}_1 \cdot \mathbf{q}}{k_1 q} \right)$. In obtaining Equation (11), we have averaged $(\mathbf{E} \cdot \mathbf{q})^2$ over the azimuthal angle ϕ with \mathbf{k}_1 as the polar axis; similarly, $(\mathbf{E} \cdot \mathbf{k}_1)$ was substituted for being its value that is obtained later on integrating over $(d^3 \mathbf{k}_1)$.

We now have

$$P_{(s)}^{(r)}(E_1)_{sd} = \frac{e^2 \hbar^2 m_d E^2 \bar{w}_d k_1}{48 \pi^2 m_s^2 (\hbar \omega)^4} \left(1 + \frac{m_s}{m_d}\right)^2 \int_{q_m}^{q_0} q \, dq \, G_{sd}^{(r)}(q) \quad \text{VI-(16)}$$

$$\times \left[1 + \left(\frac{q}{k_1}\right)^2 / \left(1 + \frac{m_d}{m_s}\right)^2 \right] [1 - F(E_1 - rE_q - s\hbar\omega)]$$

where \bar{w}_d is the weight factor which comes from the density of states of the d-band, and is the same as that used by Wilson (1938), and where $G^{(r)}(q)$ and E_q have been assumed to be independent of the angular variables. As in Chapter IV, we shall assume that most of the contributions to Equation (16) come from those electrons which are in the neighborhood of the Fermi level, so that k_1 in the numerator and k_1^2 in [...] in Equation (16) may be replaced by the Fermi momentum k_s .

Now, we need to average Equation (16) over all the initial occupied states in the s-band using the Fermi function $F(E_1)$ for the s-band, and we have

$$\begin{aligned}
 \langle P_{(s)}^{(r)} (s \rightarrow d) \rangle &= \frac{\sum_{\underline{k}_1} P_{(s)}^{(r)}(E_1)_{sd} F(E_1)}{\sum_{\underline{k}_1} F(E_1)} \\
 &= \frac{e^2 E^2 D_{sd} (K \Theta_s)^2}{32 \pi^2 m_s k_s E_F u_L^5 (\hbar \omega)^4} \left(\frac{m_d}{m_s} \right) \left(1 + \frac{m_s}{m_d} \right)^2 \int_{K \Theta_M}^{K \Theta} E_q^2 dE_q \binom{1+N(q)}{N(q)} \\
 &\quad \times \left[1 + \left(\frac{E_q}{K \Theta_s} \right)^2 / \left(1 + \frac{m_d}{m_s} \right)^2 \right] F_{(s)}^{(r)}(q)
 \end{aligned}
 \tag{VI-17}$$

where

$$\begin{aligned}
 D_{sd} &= \left(\frac{\pi \hbar^2 g_{sd}^2 \omega_d}{N_p M} \right) \\
 \beta F_{(s)}^{(r)}(q) &= \int_{-\infty}^{+\infty} dz \frac{e^z}{1+e^z} \frac{1}{1+e^{z+a}} \\
 &= \left(\frac{a}{e^a - 1} \right)
 \end{aligned}
 \tag{VI-18}$$

$$\begin{aligned}
 a &= \beta (r E_q + s \hbar \omega) \\
 K \Theta_m &= \hbar u_L |k_d - k_s| \\
 K \Theta_s &= \hbar u_L k_s ; \quad \beta = \frac{1}{KT}
 \end{aligned}$$

Equation (17) involves essentially the same types of

integrals as Chapter IV except for the fact that the lower limit of q-integral in Equation (17) is not necessarily equal to zero.

The net amount of power absorbed per s-electron is defined as

$$\bar{W}_{sd} = \sum_{r=(\pm)} \hbar\omega \left\{ \langle P_{(-)}^{(r)} (s \rightarrow d) - P_{(+)}^{(r)} (s \rightarrow d) \rangle \right\} \quad \text{VI-(19)}$$

If there are \bar{n}_s number of s-electrons per unit volume that are capable of making transitions to the d-band, the power absorbed per unit volume is simply \bar{n}_s times \bar{W}_{sd} . As was explained previously, \bar{n}_s of a ferromagnetic metal is not equal to the total effective number (n_s) of s-electrons, but is equal to $\frac{\chi(T)}{2}$ times n_s .

Upon combining Equation (17) with (19), and after some necessary mathematical manipulations, we finally obtain

$$\begin{aligned} & \text{(Power expenditure per unit volume)} \\ &= \bar{n}_s \bar{W}_{sd} \\ &= \frac{E^2}{2\omega^2} \frac{\bar{n}_s e^2}{m_s} \frac{\hbar^2 N_p g_{sd}^2 \bar{\omega}_d}{\sqrt{2 m_s E_F^3} M K \Theta} \cdot \left(\frac{\Theta_s}{\Theta} \right)^2 \left(\frac{m_d}{m_s} \right) \left(1 + \frac{m_s}{m_d} \right)^2 \left(\frac{T}{\Theta} \right)^3 \cdot Z(\omega, T) \end{aligned} \quad \text{VI-(20)}$$

where

$$\begin{aligned}
 Z(\omega, T) = & \frac{e^{\mu} \sinh \mu}{\mu} \left[\bar{J}_3(\mu, \alpha) - \frac{(e^{\mu}-1)^2}{(e^{2\mu}-1)} \mu [\bar{J}_2(\mu, \alpha) + 2\bar{K}_2(\mu, \alpha)] \right. \\
 & \left. + \left(\frac{T}{\Theta_s} \right)^2 \frac{1}{\left(1 + \frac{m_d}{m_s} \right)^2} \left\{ \bar{J}_5(\mu, \alpha) - \frac{(e^{\mu}-1)^2}{(e^{2\mu}-1)} \mu [\bar{J}_4(\mu, \alpha) + 2\bar{K}_4(\mu, \alpha)] \right\} \right] \\
 & ; \quad \mu = \beta \hbar \omega \quad ; \quad \alpha = \beta K \Theta
 \end{aligned}
 \tag{VI-(21)}$$

where \bar{J}_n and \bar{K}_n are exactly the same as J_n and K_n defined in Chapter IV except for the fact that we now have the lower limit of these integrals different from zero: the bars represent such a cut-off at the lower limit. Thus, with the definition of the cut-off

$$\alpha_M = \beta K \Theta_M
 \tag{VI-(22)}$$

we have

$$\begin{aligned}
 \bar{J}_n(\mu, \alpha) &= \int_{\alpha_M}^{\alpha} y^n dy / (e^y - e^{\mu}) (e^{\mu} - e^{-y}) \\
 \bar{K}_n(\mu, \alpha) &= \int_{\alpha_M}^{\alpha} y^n dy / (e^y - e^{\mu}) (e^{\mu} - e^{-y}) (e^y - 1)
 \end{aligned}
 \tag{VI-(23)}$$

and similarly, we define the functions $\bar{J}_n^o(\alpha)$ and $\bar{K}_n^o(\alpha)$ such that

$$\begin{aligned}\bar{J}_n^o(\alpha) &= \lim_{\mu \rightarrow 0} \bar{J}_n(\mu, \alpha) = \int_{\alpha_M}^{\alpha} y^n dy / (e^y - 1)(1 - e^{-y}) \\ \bar{K}_n^o(\alpha) &= \lim_{\mu \rightarrow 0} \bar{K}_n(\mu, \alpha) = \int_{\alpha_M}^{\alpha} y^n dy / (e^y - 1)^2 (1 - e^{-y})\end{aligned}\tag{VI-24}$$

The dispersion properties that result from Equations (20) and (21) will be obtained in the following part of this chapter. It will be shown that the d.c. damping coefficient that is obtained from Equation (20) agrees exactly with that which was obtained in the theory of the d.c. conductivity by Wilson (1936, 1938).

VI-C Damping Coefficient and Quantum Correction Factor
for Interband Transitions

Calculations of the damping coefficient $\Gamma_{ep}(\mu, \alpha)$ and $\Gamma_{ep}^0(\alpha)$ for the $s \rightarrow d$ transitions are carried out in exactly the same way as in Chapter IV, and therefore various arguments pertaining to the particular method that is employed in the present theory for computing these quantities shall not be repeated.

Upon using Equation (20) in the relation

$$\frac{E^2}{2} \sigma(\mu, \alpha) = \bar{n}_s \bar{W}_{sd} \quad \text{VI-(25)}$$

we obtain the following expression for the frequency- and temperature-dependent damping coefficient $\Gamma_{ep}(\mu, \alpha)$;

$$\Gamma_{ep}(\mu, \alpha) = \frac{9\pi^3}{2} \left(\frac{\bar{n}_s}{n_s} \right) \frac{\hbar^2 N_p g_{sd}^2 \bar{w}_d}{\sqrt{2 m_s E_F^3} M K \Theta} \left(\frac{m_d}{m_s} \right) \left(1 + \frac{m_s}{m_d} \right)^2 \left(\frac{\Theta_s}{\Theta} \right)^2 \frac{1}{\alpha^3} Z(\mu, \alpha) \quad \text{VI-(26)}$$

where (\bar{n}_s/n_s) is the ratio of the effective number of s -electrons which are capable of making the $s \rightarrow d$ transitions over the total effective number of s -electrons, and for a ferromagnetic metal, may be expressed generally in the form,

$$\begin{aligned} \left(\frac{\bar{n}_s}{n_s} \right) &= \frac{1}{2} \chi(T) \\ &= \frac{1}{2} \left[1 + \frac{\Sigma_0 - \Sigma}{\Sigma_0} \right] \end{aligned} \quad \text{VI-(27)}$$

The numerical values of $\chi(T)$ are available in Table VIII and Table X for Ni, Fe, Co and others. For a paramagnetic transition metal, \bar{n}_s is equal to n_s and $\chi(T) = 2$. The same is true for a ferromagnetic metal when temperature is well beyond the Curie temperature θ_C . For a ferromagnetic metal, the quantity of Equation (27) is most important at very low temperatures at which it is nearly equal to $(\frac{1}{2})$. As a result of this, a ferromagnetic metal has a smaller resistivity at low temperatures than a paramagnetic metal if both have the same values for other parameters.

Just as in Chapter IV, the frequency- and temperature-dependent function $Z(\mu, \alpha)$ of Equation (21) has the property,

$$Z(\mu, \alpha) = Z(-\mu, \alpha) \quad \text{VI-(28)}$$

and is independent of frequency in the limiting cases of $\mu \ll \alpha$ and $\mu \gg \alpha$, being a slowly varying function of μ for all values of ω and T except for the case of $1 \ll \mu \ll \alpha$. It is easily shown that $Z(\mu, \alpha)$ acquires the following forms in the two limiting cases;

$$Z(\mu, \alpha) \approx \left\{ \bar{J}_3^0(\alpha) + \left(\frac{T}{\Theta_s} \right)^2 \frac{1}{\left(1 + \frac{m_d}{m_s} \right)^2} \bar{J}_5^0(\alpha) \right\} ; \mu \ll \alpha, 1 \quad \text{VI-(29)}$$

$$\begin{aligned} \tilde{Z}(\mu, \alpha) \approx & \left[\frac{1}{3} \alpha^3 \left\{ 1 - \left(\frac{\alpha_M}{\alpha} \right)^3 \right\} + 2 \int_{\alpha_M}^{\alpha} \frac{x^2 dx}{e^x - 1} + \left(\frac{T}{\Theta_s} \right)^2 \frac{1}{\left(1 + \frac{m_d}{m_s} \right)^2} \right. \\ & \times \left. \left[\frac{1}{5} \alpha^5 \left\{ 1 - \left(\frac{\alpha_M}{\alpha} \right)^5 \right\} + 2 \int_{\alpha_M}^{\alpha} \frac{x^4 dx}{e^x - 1} \right] \right] ; \mu \gg \alpha \quad \text{VI-(30)} \end{aligned}$$

both of which are independent of μ and hence of ω , where $\bar{J}_3^0(\alpha)$ and $\bar{J}_5^0(\alpha)$ are given by Equation (24). Upon using Equation (29) in (26), the d.c. damping coefficient $\Gamma_{ep}^0(\alpha)$ is found as

$$\begin{aligned} \Gamma_{ep}^0(\alpha) = & \frac{9\pi^3}{2} \left(\frac{\bar{n}_s}{n_s} \right) \frac{\hbar^2 N_p g_{sd}^2 \bar{\omega}_d}{\sqrt{2} m_s E_F^3 M K \Theta} \left(\frac{m_d}{m_s} \right) \left(1 + \frac{m_s}{m_d} \right)^2 \left(\frac{\Theta_s}{\Theta} \right)^2 \frac{1}{\alpha^3} \\ & \times \left\{ \bar{J}_3^0(\alpha) + \left(\frac{T}{\Theta_s} \right)^2 \frac{1}{\left(1 + \frac{m_d}{m_s} \right)^2} \bar{J}_5^0(\alpha) \right\} \quad \text{VI-(31)} \end{aligned}$$

This agrees exactly with that calculated by Wilson (1938) when we take $\left(\frac{m_s}{m_d} \right)$ to be much smaller than unity and equate (\bar{n}_s/n_s) to unity. For most of transition metals, m_s

is actually much smaller than m_d and ignoring the terms containing the factor $\left(\frac{m_s}{m_d}\right)$ is well justified: e.g., for the triad of transition metals, Ni, Pt, and Pd, we have $\left(\frac{m_s}{m_d}\right) \sim 0\left(\frac{1}{10}\right)$ and for Nb, $\left(\frac{m_s}{m_d}\right) \sim 0(10^{-2})$. Thus, it is sufficient to take $Z(\mu, \alpha)$ and $\Gamma_{ep}(\alpha)$ in the form,

$$Z(\mu, \alpha) \cong \frac{e^\mu \sinh \mu}{\mu} \left[\bar{J}_3(\mu, \alpha) - \frac{\mu(e^\mu - 1)^2}{(e^{2\mu} - 1)} \left(\bar{J}_2(\mu, \alpha) + 2 \bar{K}_2(\mu, \alpha) \right) \right] \quad \text{VI-(32)}$$

$$\Gamma_{ep}^o(\alpha) \cong \frac{9\pi^3}{2} \left(\frac{\bar{n}_s}{\bar{n}_s} \right) \frac{\hbar^2 N_p g_{sd}^2 \omega_d}{\sqrt{2 m_s E_F^3} M K \Theta} \left(\frac{m_d}{m_s} \right) \left(\frac{\Theta_s}{\Theta} \right)^2 \frac{1}{\alpha^3} \bar{J}_3^o(\alpha) \quad \text{VI-(33)}$$

$$\bar{Z}(\mu, \alpha) \approx \left[\frac{1}{3} \alpha^3 \left\{ 1 - \left(\frac{\alpha_M}{\alpha} \right) \right\} + 2 \int_{\alpha_M}^{\alpha} \frac{x^2 dx}{e^x - 1} \right] \quad \text{VI-(34)}$$

According^{to} the results of Chapter IV, that part of the damping which originates in the intraband $s \rightarrow s$ transitions may be written in the form

$$\begin{aligned} \Gamma_{ep}^o(\alpha) \Big|_{s \rightarrow s} &= \frac{9\pi^3}{2} \frac{\hbar^2 N_p g_{ss}^2}{\sqrt{2 m_s E_F^3} M K \Theta} \cdot \frac{1}{\alpha^5} J_5^o(\alpha) \\ &= R_{ss} \frac{1}{\alpha^5} J_5^o(\alpha) \end{aligned} \quad \text{VI-(35)}$$

Then, for a comparison of the contributions by the $s \rightarrow d$ and $s \rightarrow s$ transitions, we have the ratio

$$\frac{r_{ep}^o(\alpha) \big|_{s \rightarrow d}}{r_{ep}^o(\alpha) \big|_{s \rightarrow s}} \cong \left(\frac{\bar{n}_s}{n_s} \right) \left(\frac{m_d \bar{w}_d}{m_s} \right) \left(\frac{\theta_s}{T} \right)^2 \frac{\bar{J}_3^o(\alpha)}{J_5^o(\alpha)} \quad \text{VI-(36)}$$

where we have put $g_{sd}^2 \cong g_{ss}^2$. Since we know that k_s is of the same order of magnitude as q_o , we have $\theta_s \approx \theta$ in order of magnitude. At room temperature, the ratio is mostly due to $\left(\frac{m_d \bar{w}_d}{m_s} \right)$ while, at very low temperatures, the ratio can take on a very large value. For nickel, the data on the electronic specific heat show that $\left(\frac{m_d \bar{w}_d}{m_s} \right) \approx 10$.

By dividing Equation (21) by (29) and ignoring the terms containing $\left(\frac{m_s}{m_d} \right)$ we find the following as the b-factor for transition metals;

$$b_{ep}(\mu, \alpha) = \frac{e^\mu \sinh \mu}{\mu \bar{J}_3^o(\alpha)} \left[\bar{J}_3(\mu, \alpha) - \mu \frac{(e^\mu - 1)^2}{(e^{2\mu} - 1)} \left(\bar{J}_2(\mu, \alpha) + 2 \bar{K}_2(\mu, \alpha) \right) \right] \quad \text{VI-(37)}$$

This satisfies the correspondence requirement,

$$\lim_{\omega \rightarrow 0} b_{ep}(\mu, \alpha) = 1 \quad \text{VI-(38)}$$

In the near infrared limit of $\mu \gg \alpha$, we have

$$\begin{aligned} \tilde{b}_{ep}(\mu, \alpha) = \frac{2}{3} & \left[1 + \frac{1}{\bar{J}_3(\alpha)} \left[\frac{1}{2} \alpha^3 \left\{ 1 - \left(\frac{\alpha_M}{\alpha} \right)^3 \right\} \right. \right. \\ & \left. \left. + \frac{\alpha^3}{e^{\alpha-1}} \left\{ 1 - \left(\frac{\alpha_M}{\alpha} \right)^3 \frac{e^{\alpha-1}}{e^{\alpha_M-1}} \right\} \right] \right] \end{aligned} \quad \text{VI-(39)}$$

VI-D Dispersion Properties of Transition Metals

The results of the preceding chapter allow us to write down the optical conductivity $\sigma(\mu, \alpha)$ in the form,

$$\sigma(\mu, \alpha) = \frac{n_s e^2}{m_s} \Gamma_s / (\omega^2 + \Gamma_s^2) \quad \text{VI-(40)}$$

where $\Gamma(\mu, \alpha)$ is the sum of the electron-phonon damping coefficient $\Gamma_{ep}(\mu, \alpha)$ which is given by Equation (26), and the damping terms due to the electron-electron collisions, $\Gamma_{ee}(\mu, \alpha)$, and that due to the impurity scattering, Γ_M^0 . Equation (40) includes only the contribution of the s-electrons; the d-electron contributions as well as the intra-band transitions are neglected. When contributions of both s- and d-electrons need be considered, Equation (40) may be replaced by the more general form,

$$\sigma(\mu,) = \left(\frac{n_s e^2}{m_s} \Gamma_s / (\omega^2 + \Gamma_s^2) + \frac{n_d e^2}{m_d} \Gamma_d / (\omega^2 + \Gamma_d^2) \right) \quad \text{VI-(41)}$$

where the electron-phonon contributions to both Γ_s and Γ_d include the intraband transitions as well as $s \rightleftharpoons d$ transitions. In general, it is quite sufficient to take $\sigma(\mu, \alpha)$ in the form of Equation (40) and ignore the d-electron contributions as well as the intraband transitions in s- and d-bands. Therefore, it must henceforth be remembered that whenever we speak of $\Gamma_{ep}(\mu, \alpha)$ of a transition metal, we mean the one due to the $s \rightarrow d$ transitions.

The over-all b-factor for the total damping coefficient $\Gamma(\mu, \alpha)$ is again defined as

$$b(\mu, \alpha) = \left(\frac{\Gamma_{ep}^0}{\Gamma^0} b_{ep}(\mu, \alpha) + \frac{\Gamma_{ee}^0}{\Gamma^0} b_{ee}(\mu, \alpha) + \frac{\Gamma_M^0}{\Gamma^0} \right)$$

where $b_{ee}(\mu, \alpha)$, Γ_{ee}^0 , and Γ_M^0 were discussed in Chapter V, and

$$\Gamma^0 = \left(\Gamma_{ep}^0(\alpha) + \Gamma_{ee}^0(\alpha) + \Gamma_M^0 \right) \quad \text{VI- (42)}$$

The optical dielectric constant $\epsilon(\mu, \alpha)$ is obtained from Equation (40) by using the Kramers-Kronig relation. The relevant mathematical arguments which were applied in solving the Kramers-Kronig relation in Chapter V are just as applicable to transition metals, and thus will not be repeated here.

With the definition of the temperature-dependent quantity $\bar{\beta}(\alpha)$ such that

$$\bar{\beta}(\alpha) = b_{ep}(i\mu_0 \bar{\beta}, \alpha) = R_e b_{ep}(i\mu_0 \bar{\beta}, \alpha) \quad \text{VI-(43)}$$

the optical dielectric constant is given by

$$\begin{aligned} [1 - \epsilon(\mu, \alpha)] &= \frac{\omega_o^2}{\omega^2 + (\bar{\beta} \Gamma^o)^2} \\ \therefore \frac{\omega_o^2}{4\pi} &= \left(\frac{n_s e^2}{m_s} \right) \end{aligned} \quad \text{VI-(44)}$$

Thus, all the relations of Chapter V should be applicable to transition metals when we replace b_{ep} and β_{ep} of Chapter IV by those given by (37) and (43), respectively.

The difference between the results of Chapter IV on non-transition metals and the results of the present chapter on transition metals are exhibited most strongly at low temperatures and in the near infrared. Some of these properties will be discussed.

VI-E Some Low-Temperature and Near Infrared Properties of Transition Metals:

For the discussion on low-temperature and near infrared properties of transition metals and comparison of these properties with the properties of non-transition metals, it is convenient to define a constant R_{ep}^{sd} given by

$$\frac{q\pi^3}{2} \frac{\hbar^2 N_p}{\sqrt{2} m_s E_F^3} \frac{g_{sd}^2 \bar{w}_d}{M K \Theta} \left(\frac{m_d}{m_s} \right) \left(1 + \frac{m_s}{m_d} \right)^2 \left(\frac{\Theta_s}{\Theta} \right)^2 \quad \text{VI-(45)}$$

Then, the electron-phonon damping coefficient that was obtained in (26) can be written as

$$\begin{aligned} \Gamma_{ep}(\mu, \alpha) &= R^{sd} \left(\frac{\bar{n}_s}{n_s} \right) \frac{1}{\alpha^3} Z(\mu, \alpha) \\ &\cong R^{sd} \left(\frac{\bar{n}_s}{n_s} \right) \frac{1}{\alpha^3} \bar{J}_3^o(\alpha) b_{ep}(\mu, \alpha) \end{aligned} \quad \text{VI-(46)}$$

where b_{ep} is that given by (37)

First, let us investigate the low-temperature behavior of $\Gamma^o(\alpha)$. According to (46), we have

$$\Gamma_{ep}^o(\alpha) \cong R^{sd} \left(\frac{\bar{n}_s}{n_s} \right) \frac{1}{\alpha^3} \bar{J}_3^o(\alpha) \quad \text{VI-(47)}$$

In the limit, $\alpha \gg 1$, this becomes

$$\begin{aligned} \Gamma_{ep}^o &\approx R^{sd} \left(\frac{\bar{n}_s}{n_s} \right) \frac{e^{-\alpha_M}}{\alpha^3} \left[\alpha_M^3 + 3\alpha_M^2 + 6\alpha_M + 6 \right] \\ &= 6 R^{sd} \left(\frac{\bar{n}_s}{n_s} \right)_o \left(\frac{T}{\Theta} \right)^3 : \alpha_M = 0 \end{aligned} \quad \text{VI-(48)}$$

$$= R^{sd} \left(\frac{\Theta_s}{\Theta} \right)^3 \left(\frac{\bar{n}_s}{n_s} \right)_o e^{-\alpha_M} : \alpha_M > 0 \quad \text{VI-(49)}$$

where

$$\left(\frac{\bar{n}_s}{n_s} \right) = \begin{cases} \frac{1}{2} & : \text{ferromagnetic metal} \\ 1 & : \text{paramagnetic metal} \end{cases}$$

and $\left(\frac{\Theta_s}{\Theta} \right)$ is of the order of unity since k_s is in general of the same order as the Debye's cut-off value q_o . For most of transition metals, α_M is not equal to zero, and hence the equation (49) is to be used. For these metals, the electron-phonon damping coefficient vanishes like $\sim e^{-\alpha_M}$, when T is decreased to the absolute zero. The negative exponential factor was also obtained by Wilson (1938). On the other hand, the damping contributed by the electron-electron collisions and the impurity scattering was shown in the previous chapter to be of the form,

$$\left(\Gamma_{ee}^o(\alpha) + \Gamma_M^o \right) = \left(R_{ee} \left(\frac{T}{\Theta} \right)^2 + \Gamma_M^o \right) \quad \text{VI-(50)}$$

where R_{ee} and Γ_M° are nearly independent of T , and R_{ee} is in general much smaller than R_{ep} .

Therefore, for metals with α_M different from zero, the over-all d.c. damping coefficient at very low temperatures retains only that part which is given by (50), despite the fact that the electron-phonon part alone constitutes the most of $\Gamma^{\circ}(\alpha)$ at higher temperatures. This explains the T^2 -dependence of resistivity of some transition metals which has been observed by various experimenters. We summarize the above discussion by writing down Γ° as

$$\Gamma^{\circ}(\alpha) \approx \left(R_{ee} \left(\frac{T}{H} \right)^2 + \Gamma_M^{\circ} \right) : \left(\begin{matrix} \alpha \gg 1 \\ \alpha_M > 0 \end{matrix} \right)$$

VI-(51)

The same was found to be true even for a noble metal due to the rapid decrease, $\sim T^5$ of $\Gamma_{ep}^{\circ}(\alpha)$ with decrease in temperature, although not as rapid as in (49).

Whether there is a transition metal with $\alpha_M = 0$ is a question that is yet to be answered. For such a metal, the $s \longrightarrow d$ transitions at the Fermi level can take place without a finite momentum transfer implying that phonons with the average energy of the order of $\sim (KT)$ are capable of stimulating the $s \longrightarrow d$ transitions even at a very low temperature. The following discussion based on a rather qualitative description of the properties of the s - and d -

bands suggests that, out of all transition metals and likewise of all multivalent metals for which interband transitions are important, there can exist a metal with $\alpha_M = 0$ if the electrons in the outer band (s- band) are neither more nor less in number than what is required to completely close the empty states of the inner band (d- band) that is involved in the interband transitions. Three transition metals which do satisfy such a condition are the triad, N_i , P_t , and P_d . For nickel, the three possible configurations are $(3d^8 4s^2)$, $(3d^9 4s^1)$, and $(3d^{10} 4s^0)$. For platinum, they are the configurations, $(5d^8 6s^2)$, $(5d^9 6s^1)$, and $(5d^{10} 6s^0)$. For palladium, they are the configurations, $(4d^9 5s^1)$ and $(4d^{10} 5s^0)$. In all three metals, the s-electrons plus the d-electrons amount to 10 electrons which can exactly close the d-band. Further, it is known that all three metals have an approximately 0.6 electrons per atom in the s-band and the same number of holes in the d-band. That these metals can have

$$\alpha_M = 0$$

and hence

$$k_d = k_s$$

may be shown by computing the total number of empty states in the d-band and the total number of s-electrons from the density-of-states functions of the two bands. At very low temperature, the Fermi function $(F(E))$ is nearly equal to unity, and we have

$$n_s = \int_0^{E_F} \rho_s(E) dE \quad ; \quad n_d^o = \int_{E_F}^{E_o} \rho_d(E) dE \quad \text{VI-(52)}$$

where n_d^o is the number of empty states in the d-band and the density-of-states functions $\rho_s(E)$ and $\rho_d(E)$ are given by

$$\begin{aligned} \rho_s(E) &= \frac{\sqrt{2}}{\pi^2} \left(\frac{m_s}{\hbar^2} \right)^{3/2} \sqrt{E} \\ \rho_d(E) &= \frac{\sqrt{2}}{\pi^2} \left(\frac{m_d}{\hbar^2} \right)^{3/2} \sqrt{E_o - E} \end{aligned} \quad \text{VI-(53)}$$

Using these in (52), we obtain

$$\begin{aligned} n_s &= \frac{1}{3\pi^2} \left(\frac{2m_s}{\hbar^2} E_F \right)^{3/2} = k_s^3 / 3\pi^2 \\ n_d^o &= \frac{1}{3\pi^2} \left(\frac{2m_d}{\hbar^2} (E_o - E_F) \right)^{3/2} = k_d^3 / 3\pi^2 \end{aligned} \quad \text{VI-(54)}$$

Therefore, we find that $k_d = k_s$ for those metals for which n_s is identically equal to n_d^o .

Although the above result may not lead us to a definite conclusion, due to the use of the simplified forms of ρ_s

ρ_d , it does permit us to suggest that, if there is any metal which has $\alpha_M = 0$, the triad of transition metals N_1 , P_t , and P_d , are the most likely ones. In fact, according

to the observations by MacDonald and Mendelssohn (1950), the low-temperature resistivity of platinum has been interpreted as having a T^2 -dependence on temperature, which, if real, may be attributed to $\Gamma_{ee}^0(\alpha)$. On the other hand, if platinum has $\alpha_M = 0$ so that equation (48) is applicable, the low-temperature resistivity should have both T^2 - and T^3 -dependence on temperature coming from Γ_{ee}^0 and Γ_{ep}^0 , respectively. The total damping coefficient will then be given by

$$\Gamma_{Pt}^0(\alpha) \approx 6 R^{sd} \left(\frac{T}{\Theta} \right)^3 + R_{ee} \left(\frac{T}{\Theta} \right)^2 + \Gamma_M^0 \quad \text{VI-(55)}$$

where the first term is not necessarily much smaller than the rest unless T is very near the absolute zero: e.g. at $\left(\frac{T}{\Theta} \right) = 1/20$, we have

$$\Gamma_{ep}^0 \sim R_{ep} \cdot 10^{-3}$$

$$\Gamma_{ee}^0 \sim R_{ee} \cdot 10^{-3}$$

and, since R_{ep} is generally larger than R_{ee} by a factor of 10 or more, Γ_{ep}^0 is not unimportant even at a temperature as low as $10 \sim 20^\circ \text{K}$.

It is not difficult to see that, even if the low-temperature resistivity exhibits the T^3 -term, a clear distinction between T^3 & T^2 -terms is not an easy task

at low temperatures, and it is thus very possible that this term has been confused with the T^2 — term in the past measurements.

Let us investigate the low temperature properties of the quantum-corrected damping coefficient $\Gamma_{ep}(\mu, \alpha)$ in the near infrared, i.e. $\mu \gg \alpha \gg 1$. The low temperature properties of $\Gamma_{ep}(\mu, \alpha)$ in the spectral ranges, $\mu \ll \alpha$ will be left to the future chapter dealing with the absorption at very low temperatures.

We saw in the previous chapters that, unlike the d.c. damping coefficient $\Gamma_{ep}^0(\alpha)$, the quantum-corrected damping coefficient maintains a relatively large value in the near infrared even at 0° K. It will be shown that a similar quality is also found in transition metals, and that this is true for all transition metals regardless of whether α_M vanishes or not provided that α_M is of a much smaller order of magnitude than α .

At very low temperatures, the b- factor for the near infrared spectrum reduces to

$$\tilde{b}_{ep}(\mu, \alpha) \approx \frac{1}{3 \bar{J}_s(\alpha)} \alpha^3 \left[1 - \left(\frac{\alpha_M}{\alpha} \right)^3 \right]$$

VI-(55)

When we use this in (46), we obtain

$$\tilde{\Gamma}_{ep}(\mu, \alpha) \approx \left(\frac{\bar{n}_s}{n_s} \right)_0 \frac{1}{3} R^{sd} \left[1 - \left(\frac{\Theta_M}{\Theta} \right)^2 \right]$$

$$\approx \frac{1}{6} R^{sd} : \text{F.M.}$$

$$\approx \frac{1}{3} R^{sd} : \text{P.M.}$$

VI-(56)

which is independent of both ω and T , where we have taken

$\Theta_M \ll \Theta$. Thus, unlike $\Gamma_{ep}^o(\alpha)$, the negative exponential factor $e^{-\alpha_M}$ cancels out, and the electron-phonon scattering makes a large contribution even at very low temperatures. This implies further that the contributions to the damping by the electron-electron collisions and impurity scattering will be important at very low temperatures in the near infrared only if they are important at higher temperatures. When these two processes need be considered, we use the formula,

$$\begin{aligned} \tilde{\Omega}_o(\mu, \alpha) &= \Gamma_{ep}^o \tilde{b}_{ep} + \Gamma_{ee}^o(\alpha) + \Gamma_M^o \\ &\cong \frac{1}{6} \chi(0) R^{sd} + R_{ee} \frac{1}{\alpha^2} + \Gamma_M^o \end{aligned}$$

$$: \alpha \gg 1$$

VI-(57)

while $\bar{\mathcal{N}}_o(\alpha)$, which appears in $\epsilon(\mu, \alpha)$, becomes

$$\begin{aligned}\bar{\mathcal{N}}_o(\alpha) &\approx R_{ee} \frac{1}{\alpha^2} + \Gamma_M^o \\ &= \Gamma_M^o : T = 0^\circ K\end{aligned}\quad \text{VI-(58)}$$

In (57), $\tilde{\mathcal{N}}_o$ has a weak T^2 -dependence while in (58),

$\bar{\mathcal{N}}_o(\alpha)$ has a relatively strong T^2 -dependence on temperature, since, in general, $R_{ep} \gg R_{ee} \gtrsim \Gamma_M^o$. As a specific example, let us investigate the near infrared absorptivity at very low temperature. According to Chapter V, the bulk absorptivity A_B is given by

$$A_B \approx \sqrt{\frac{m_s}{\pi n_s e^2}} \tilde{\mathcal{N}}_o \tilde{G}_\sigma \quad \text{VI-(59)}$$

where

$$\begin{aligned}\tilde{\mathcal{N}}_o \tilde{G}_\sigma &= \left(\tilde{\mathcal{N}}_o + \frac{\omega^2}{\mathcal{N}_{ee}} \right) \\ \mathcal{N}_{ee} &= \frac{10^{24}}{1.49} \left(\frac{\Theta^2}{R_{ee}} \right)\end{aligned}\quad \text{VI-(60)}$$

and $\tilde{\mathcal{N}}_o$ is given by (57). In general, $R_{sd} \gg R_{ee}$, and when this is true, \mathcal{N}_{ee} is also much larger than ω_o so that

$\tilde{\mathcal{N}}_o \tilde{G}_\sigma \approx \frac{1}{6} \chi(0) R^{sd}$ for a reasonably pure sample. Thus the total near infrared absorptivity A of a transition metal

is

$$A \approx \frac{1}{3} \chi(0) \frac{R_{sd}}{\omega_0} + \frac{3}{4} \frac{v_F}{c} \quad \text{VI-(61)}$$

where the second term is the absorption due to the anomalous skin effect and $v_F \cong (10^{-3} \sim 10^{-2})c$. The numerical value of R_{sd} can be determined from the room temperature value of $\epsilon_p^o(\alpha)$ since the complete temperature-dependence is specified in (47), and $\epsilon_p^o(\alpha)$ is easily found from the optical data and also from d.c. electric measurements.

The temperature-dependence characteristics that have been discussed here are to be used in various dispersion formulae that are given in Chapter V in applying the present theory to transition metals. It must be kept in mind that some transition metals exhibit resonances at relatively long wavelengths compared with noble metals, and when this happens the resonance contribution must be subtracted out of the dispersion curves, by use of the Kramers-Kronig relation or by other means, before the theory is applied. A method of subtracting the contribution of the bound electrons to the infrared dispersion was illustrated in Chapter III where we used the Kramers-Kronig relation. When the resonance band is narrow and clearly distinguishable, separation of the free-electron part of dispersion becomes a trivial matter.

Table V
Numerical Values of $J_5^{\circ}(\alpha)$

$\frac{1}{\alpha} = \frac{T}{\textcircled{H}}$	$J_5^{\circ}(\alpha)$
0	124.43
0.05	124.42
0.076923	123.14
0.1	116.38
0.125	101.48
0.16667	70.873
0.2	50.263
0.25	29.488
0.33333	12.771
0.5	3.2293
0.66667	1.1199
0.83333	0.47907
1	0.23662
1.25	0.098845
1.52	0.0451

Table VI

Temperature-dependence of Damping Coefficient

in Gold (\textcircled{H}) = 175°K)

T (°K)	$\Gamma_{ep}^{\circ}(T)/\Gamma_{ep}^{\circ}(273^{\circ})$ calculated	$\Gamma^{\circ}(T)/\Gamma^{\circ}(273^{\circ})$ observed
273	1	1
87.43	0.2645	0.2551
78.86	0.2276	0.2187
57.8	0.1356	0.1314
20.4	0.00604	0.0058
18.9	0.00346	0.0035
14.3	0.00117	0.00137
12.1	0.00051	0.00048
11.1	0.00033	0.00030
4.2	3×10^{-6}	3×10^{-6}

Table VII

Metals	$\sigma_o \times 10^{-16}$ esu (Present Theory)	$\sigma_o \times 10^{-16}$ esu (Electrical Meas.)	$\frac{\sigma_o(\text{Meas})}{\sigma_o(\text{Calc.})}$	Optical Data Used to Calculate Theoretical Value of σ_o
Al	14	15 (Meas. by B. & C.)	1.1	Beattie & Conn (1955)
	18	22 (Meas. by Golovashkin et al)	1.2	Golovashkin et al (1960)
N _i	4.8	4.6 (Meas. by B. & C.)	1.0	Beattie & Conn (1955)
G _a	3.5	3.5 (I.C.T., 1936)	1.0	Schulz (1957)
H _g	0.94	0.94 (I.C.T., 1936)	1.0	Schulz (1957)
T _i	1.6	1.64 (H. & B.)	1.0	Hass & Bradford (1957)
S _n	5	7.8 (Bulk) (Am. Inst. Phys. Hb., 1957)	1.6	Hodgson (1955)
Z _n	4 *	15 (Bulk) (Am. Inst. Phys. Hb., 1957)	3.8	Hodgson (1955)
C _u	12	13.5 (Meas. by S. & P.)	1.1	Schkliarevskii & Padalka (1959)

* The spectral range in which the optical data are available was too close to the resonance region, and hence this value is not completely reliable.

By "Bulk" is meant that σ_o values quoted are obtained for bulk samples while the optical data were taken with thin layers or mirrors.

Table VIII

	F_e		C_o, N_1		$j = \frac{1}{2}(\text{theory})$	
$\frac{T(^{\circ}\text{K})}{\Theta_c}$	$\left(\frac{\Sigma}{\Sigma_o}\right)$	$\frac{1}{2} \chi(\tau)$	$\left(\frac{\Sigma}{\Sigma_o}\right)$	$\frac{1}{2} \chi(\tau)$	$\left(\frac{\Sigma}{\Sigma_o}\right)$	$\frac{1}{2} \chi(\tau)$
0	1	0.500	1	0.500	1	0.500
0.1	0.996	0.502	0.996 *	0.502	1.000	0.500
0.2	0.99	0.505	0.99	0.505	1.000	0.500
0.3	0.975	0.512	0.98	0.510	0.997	0.501
0.4	0.95	0.525	0.96	0.520	0.983	0.508
0.5	0.93	0.535	0.94	0.530	0.958	0.521
0.6	0.90	0.550	0.90	0.550	0.907	0.546
0.7	0.85	0.575	0.83	0.585	0.829	0.585
0.8	0.77	0.615	0.73	0.635	0.710	0.645
0.85	0.70	0.650	0.66	0.670	0.630	0.685
0.9	0.61	0.695	0.56	0.720	0.525	0.737
0.95	0.46	0.770	0.40	0.800	0.380	0.810
1.00	0	1.000	0	1.000	0	1.000

* For N_1 only

Computed from the Am. Inst. Phys. Hdb.

Table IX

Theoretical Values of Microscopic Parameters

Metals	$N \left(\frac{m}{m^3} \right) \times 10^{-22}$ (cm ⁻³)	$\Gamma_{ep}^o \times 10^{-14}$ (sec ⁻¹)	\tilde{b}_{ep}	$\sigma_o \times 10^{-16}$ (esu)	$\Gamma_{ee}^o \times 10^{-12}$ (sec ⁻¹)	$v_F \times 10^{-8}$ (cm/sec)	γ ergs. cm ⁻³ / deg ²	$\gamma_R^o \times 10^{14}$ (sec.)	$\omega_o \times 10^{-15}$ (sec ⁻¹)
C _u	4.2	0.533	1.2	20	3.1	1.3	483	1.8	12
N ₁ (I)	1.2	0.625	1.24	4.8	50	0.8	424	0.9	6.2
N ₁ (II)	0.8	1.1	1.24	2.0	73	0.7	424	0.6	5.1
Al	7.1	1.12	1.2	18	4.2	2.7	718	0.9	15
Al ^o (78° K)	6.8	0.141	5.94	144	0.3	2.4	734	7	15
P _t	5.7	10.6	1.1	1.4	1.7	1.3	692	0.1	14
I _r	8.1	17.1	1.1	1.2	1.7	1.7	449	0.06	16
T ₁	2.2	3.52	1.3	1.6	---	---	---	0.3	8.4
H _g	7.65	21.4	1.00	0.94	1.2	1.55	620	0.05	16
G _a	14.6	10.7	1.07	3.5	0.28	1.88	860	0.1	22
Z _n	1.26	0.94	---	16	---	---	---	1.1	6.4
S _n	6.16	3.0	---	8	---	---	---	0.3	14

C_u, N₁(I): Beattie & Conn (1955)N₁(II) : Shkliarevskii & Padalka (1959)

All metals for room temperature except for this

 γ = Sommerfeld constant for electronic specific heat

For other references on optical data, refer to Table II and VII.

Table X

Elements	Curie Point θ_c (°C)	Σ_o	Σ (293° K)	$\frac{1}{2} \chi = \frac{1}{2} \left[1 + \frac{z_o - \Sigma}{z_o} \right]$ (293° K)
F _e	770	221.9	218.0	0.509
C _o	1131	162.5	161	0.505
N _i	358	57.50	54.39	0.527
G _d	16	253.5	0	1.000
D _y	-168	-----	0	1.00(0)

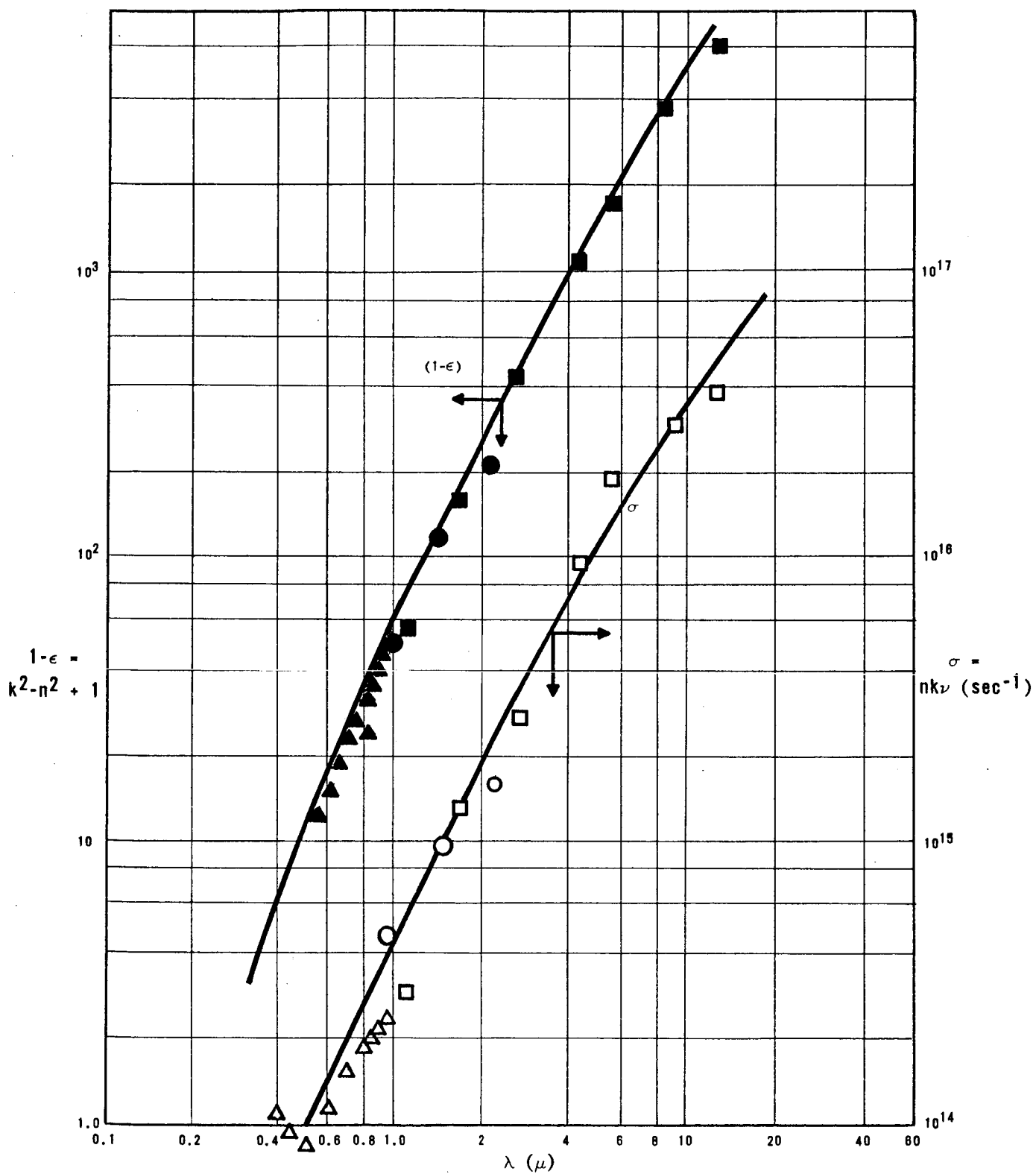


FIGURE 7

Silver

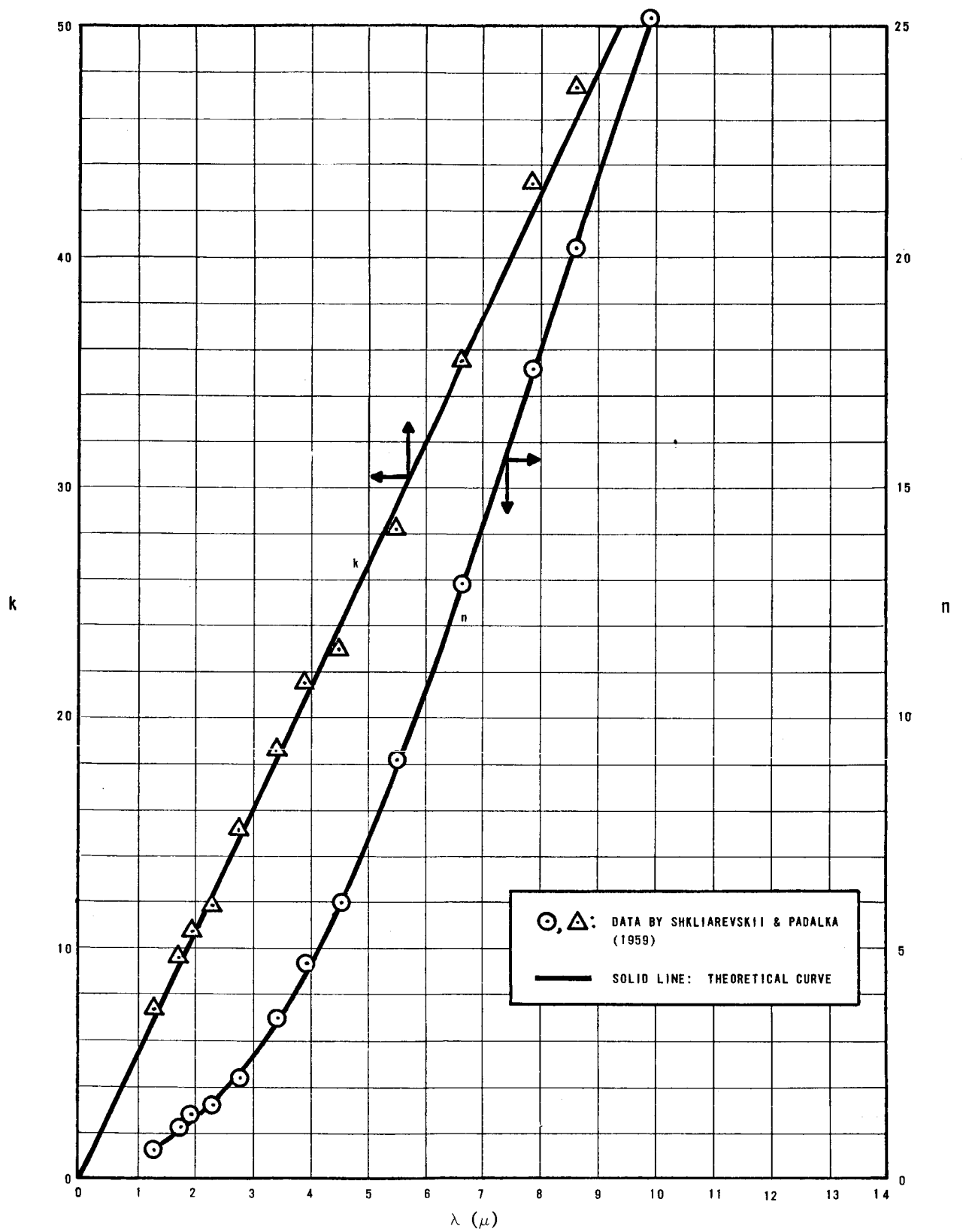


FIGURE 8

Gold ($\sim 300^\circ\text{K}$) n , k vs λ

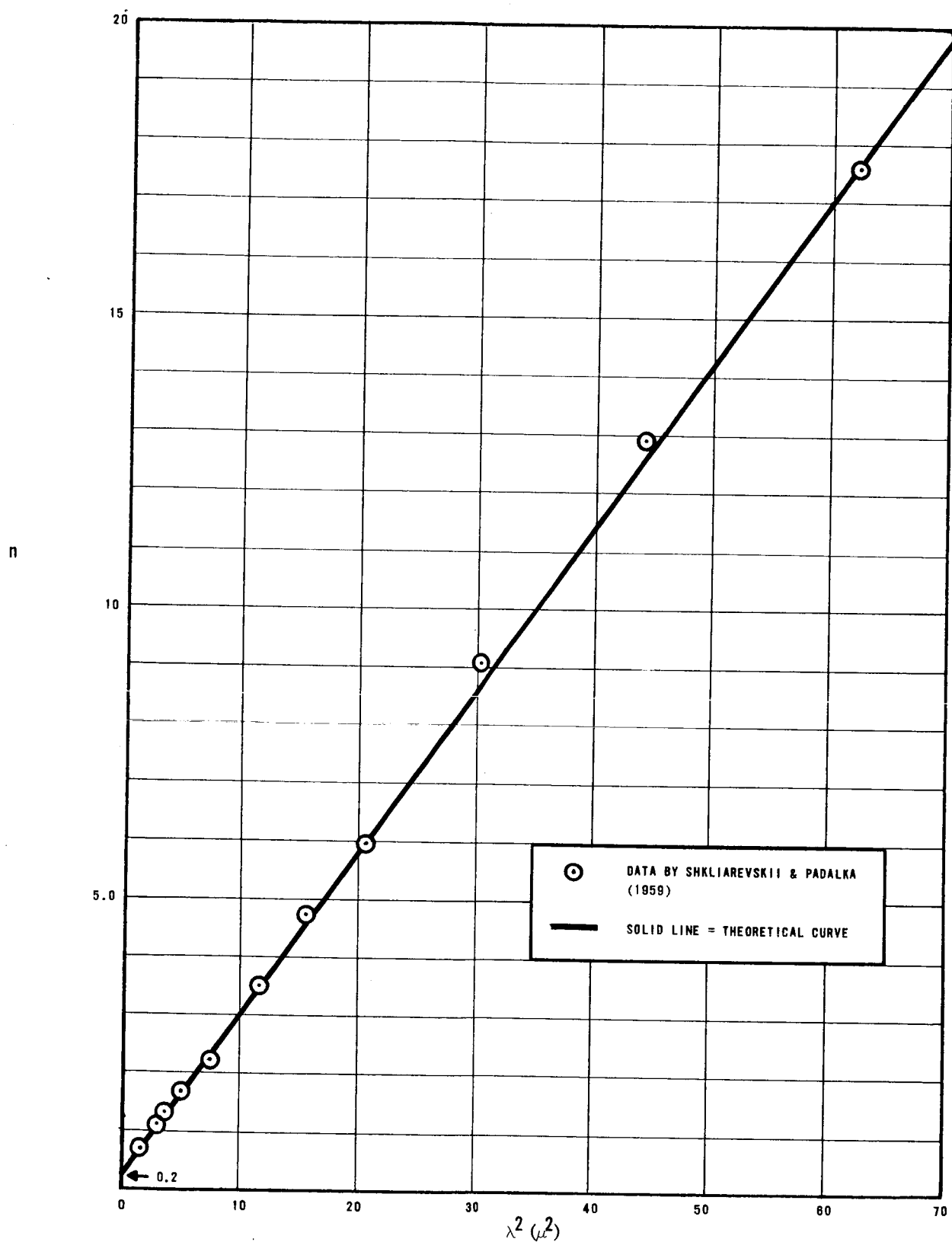


FIGURE 9

Gold ($\sim 300^\circ\text{K}$) n vs λ^2

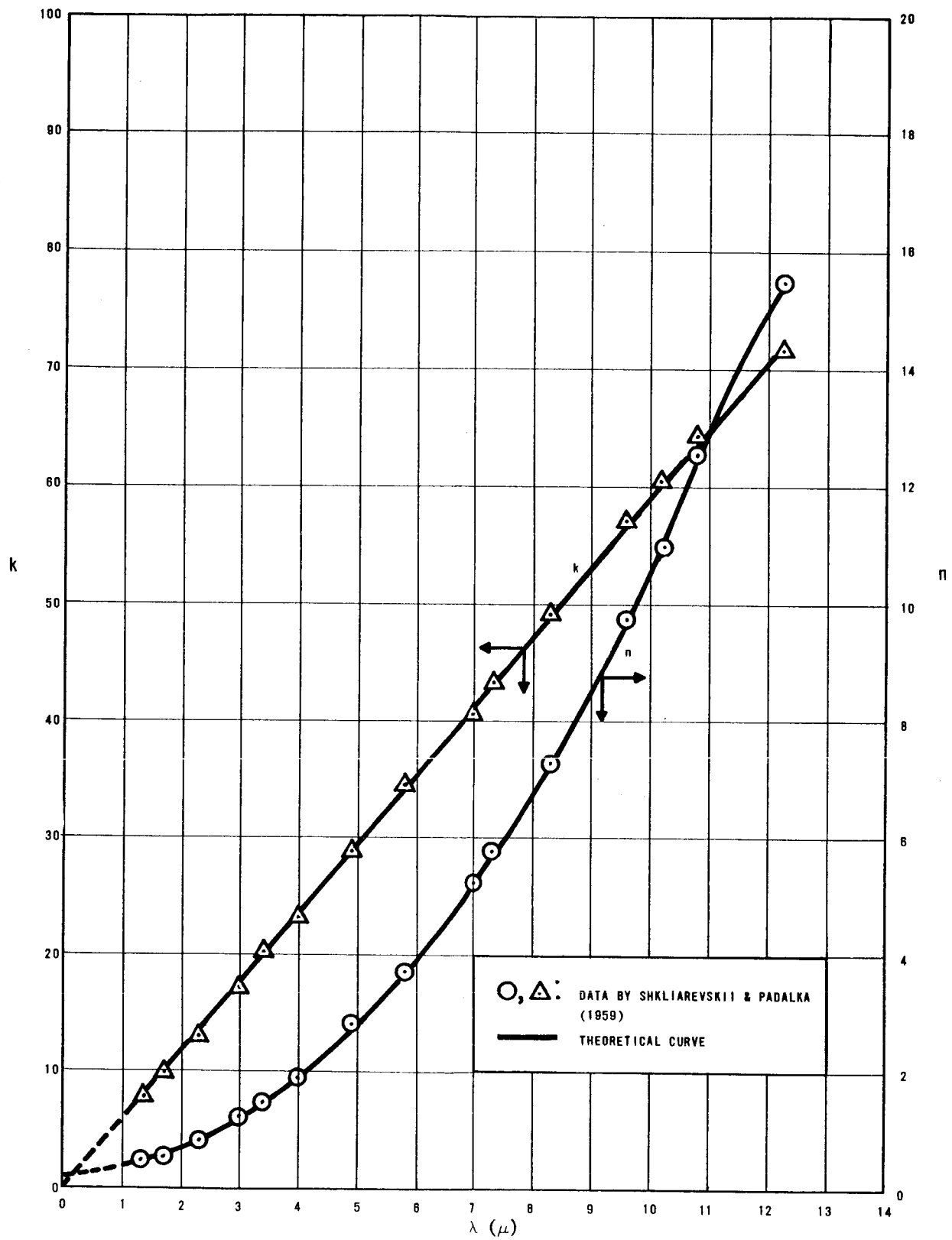


FIGURE 10

Copper ($\sim 300^\circ\text{K}$) n , k vs. λ

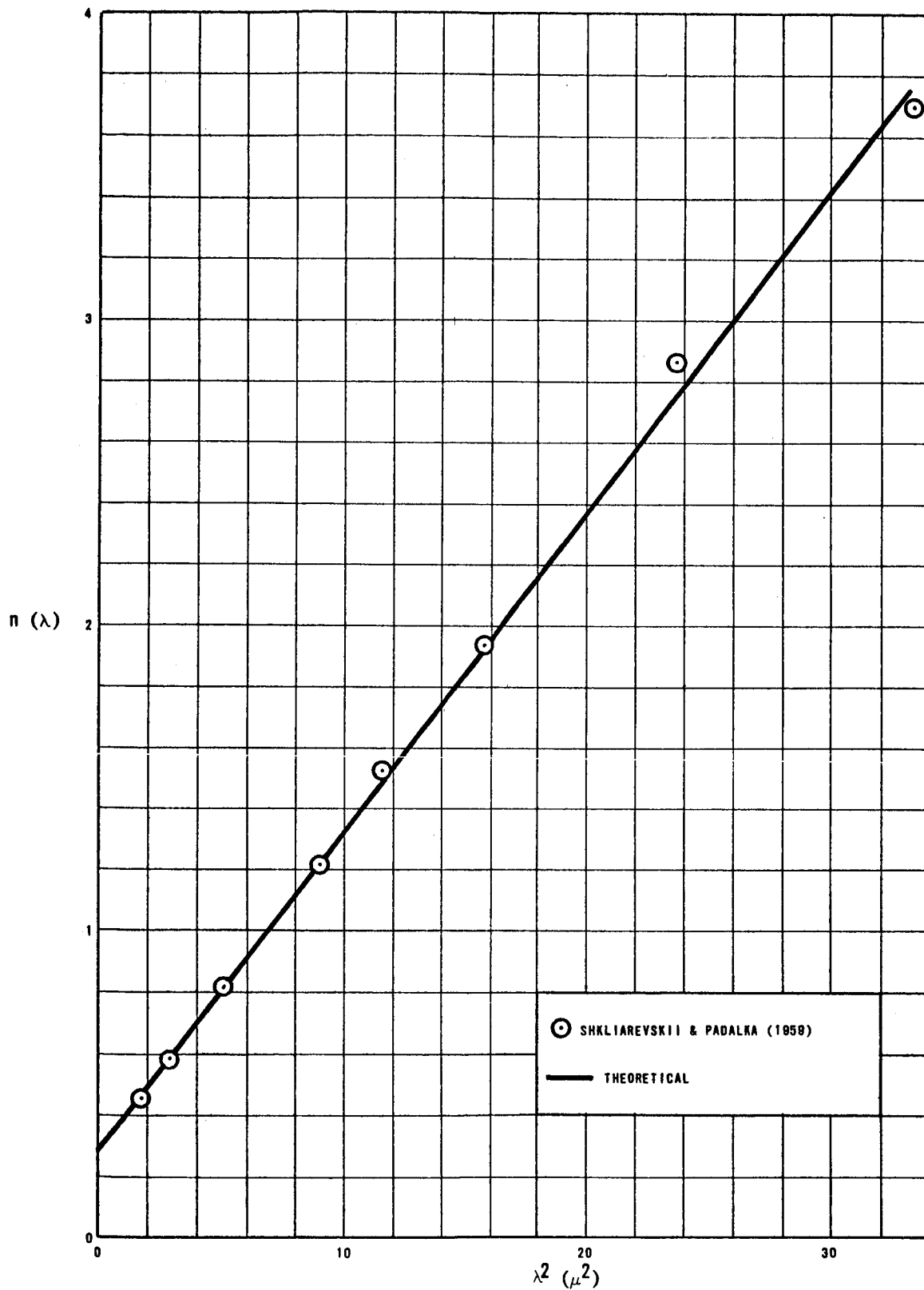
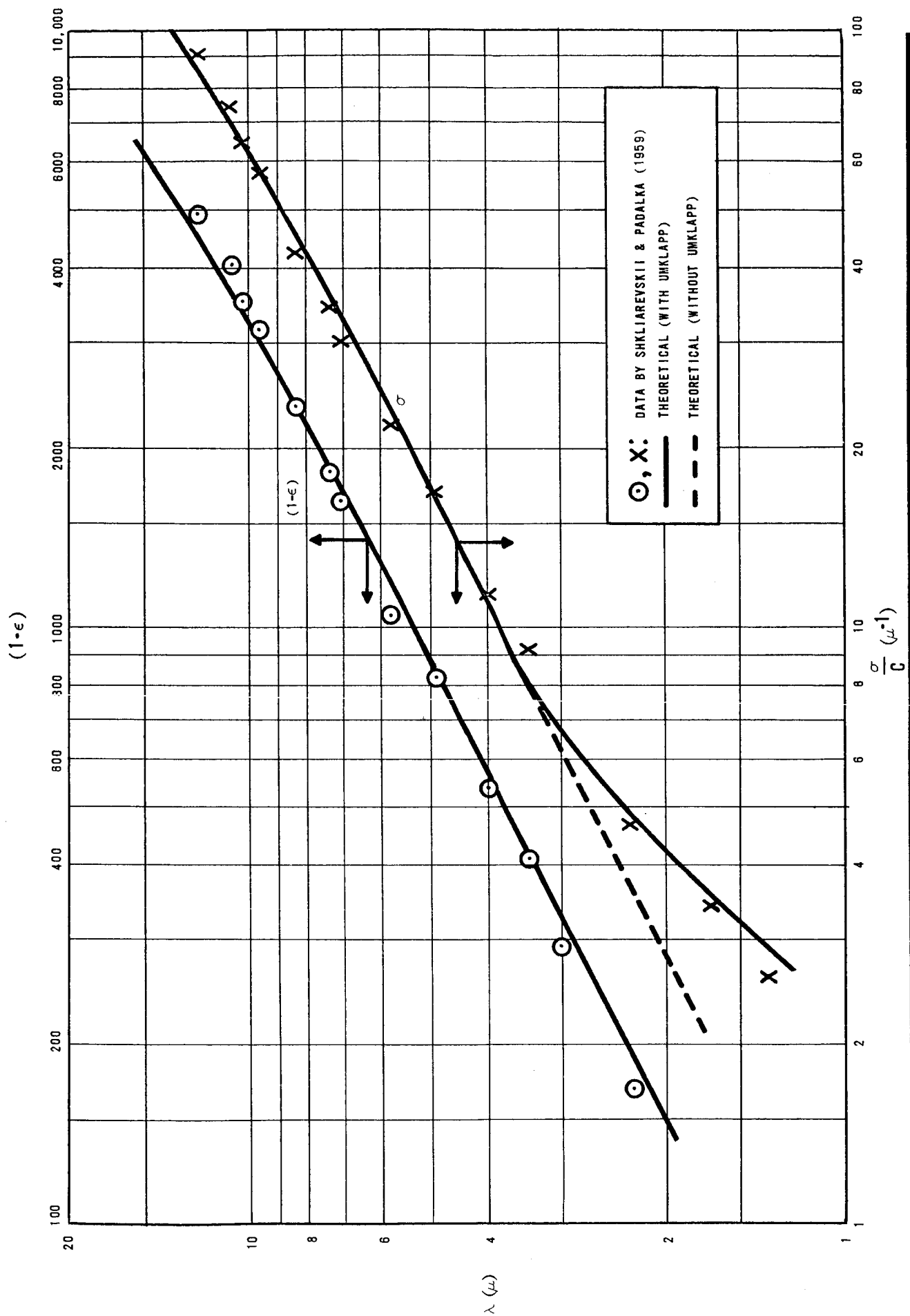


FIGURE 11

Copper ($\sim 300^\circ\text{K}$) n vs λ^2



Copper ($\sim 300^\circ\text{K}$) $(1-\epsilon)$ and $\frac{\sigma}{C}$ vs λ

FIGURE 12

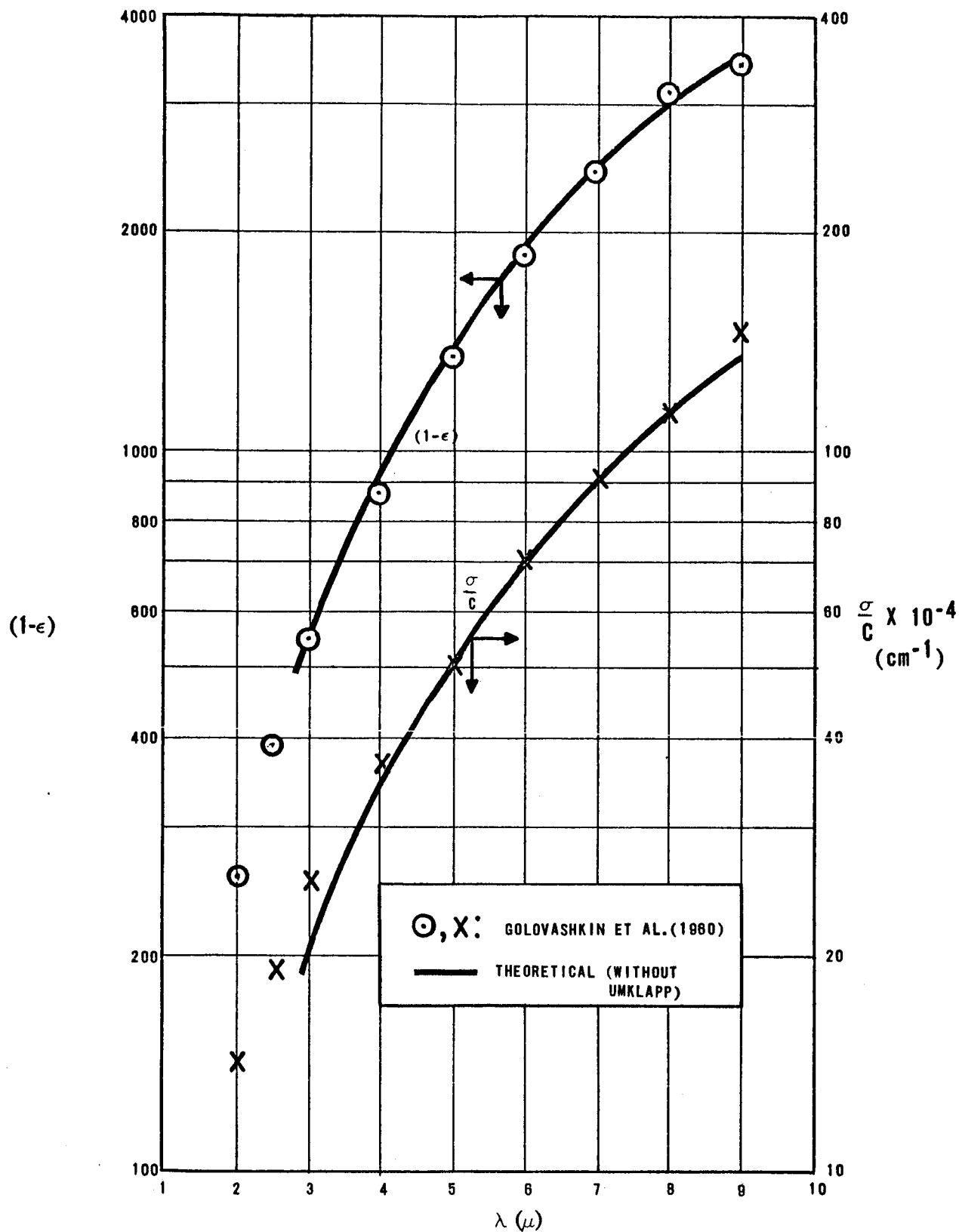


FIGURE 13

Aluminum (295°K) $(1-\epsilon)$ and $\frac{\sigma}{C}$
vs λ

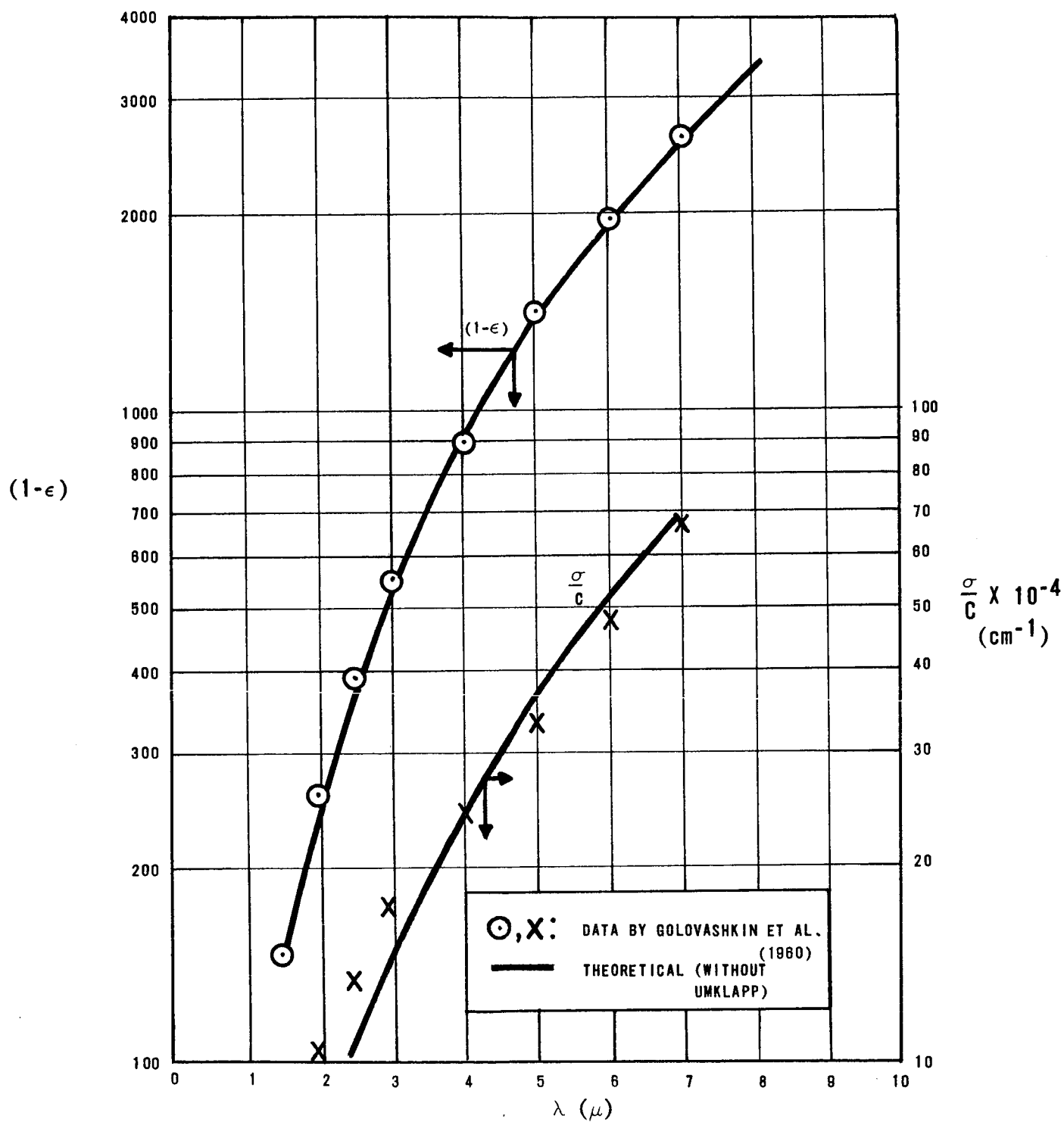


FIGURE 14

Aluminum (78°K) $(1-\epsilon)$ and $\frac{\sigma}{C}$ vs λ

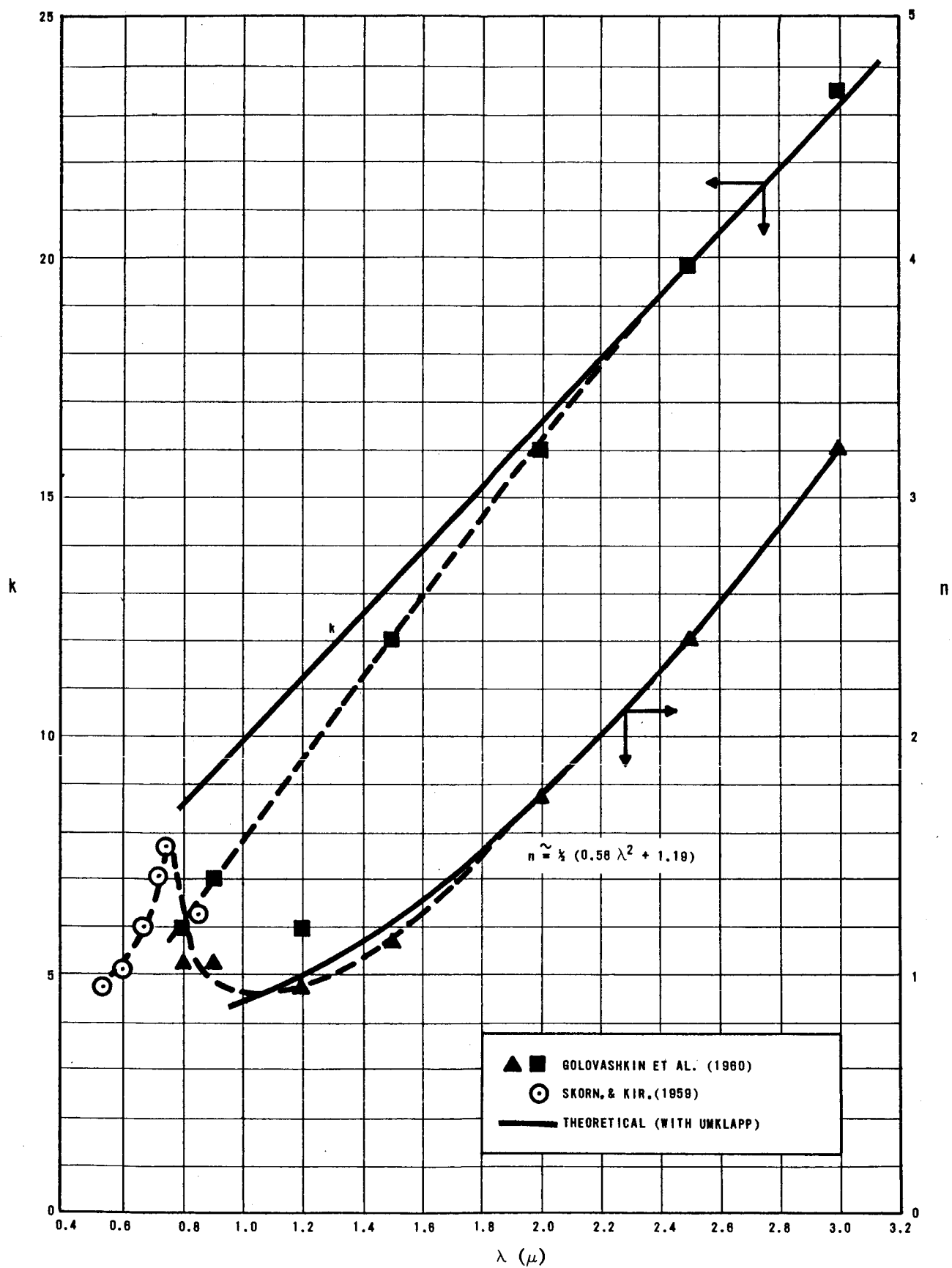


FIGURE 15

Aluminum (295° K) n , k vs λ

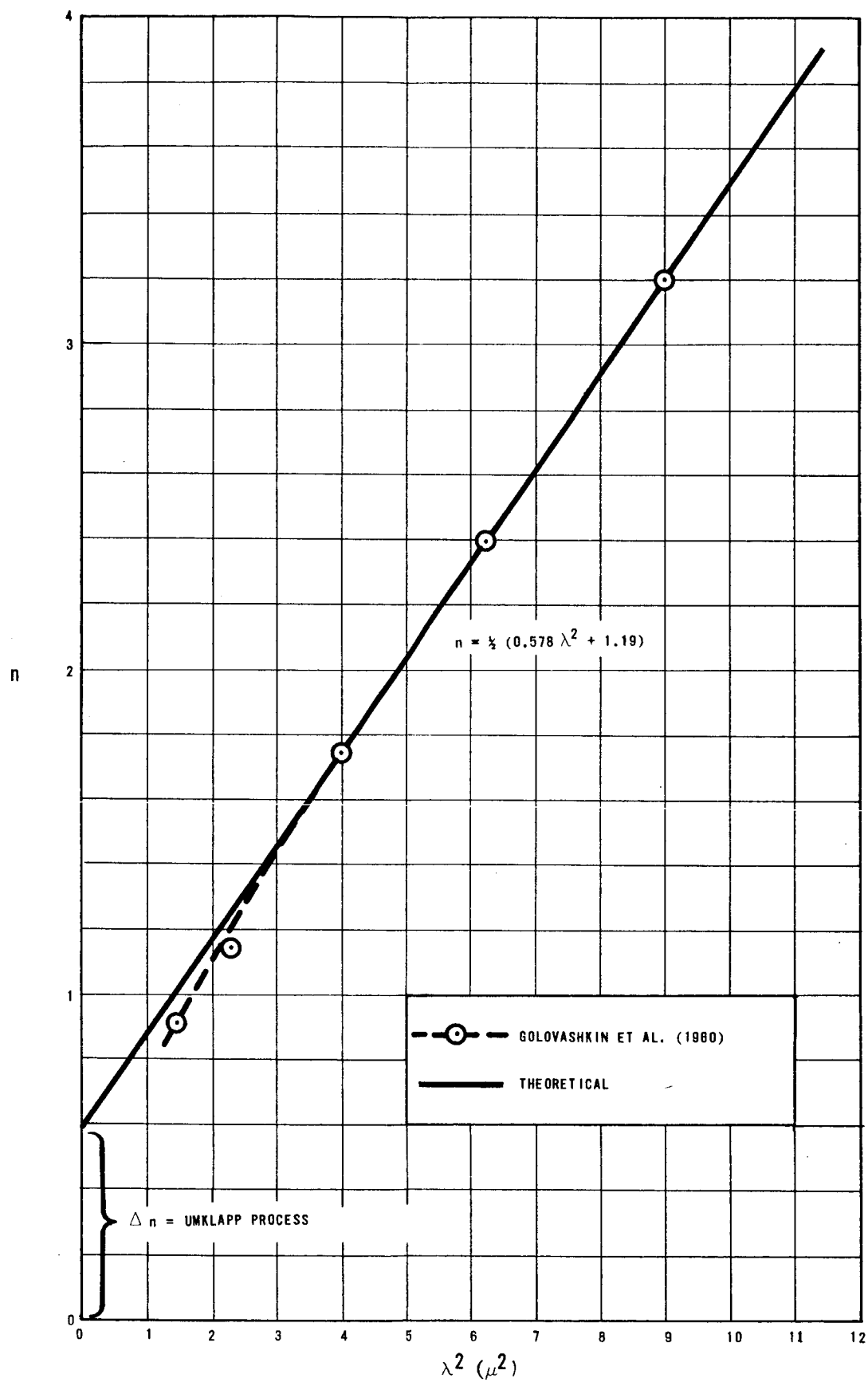


FIGURE 16

Aluminum (295°K) n vs λ^2

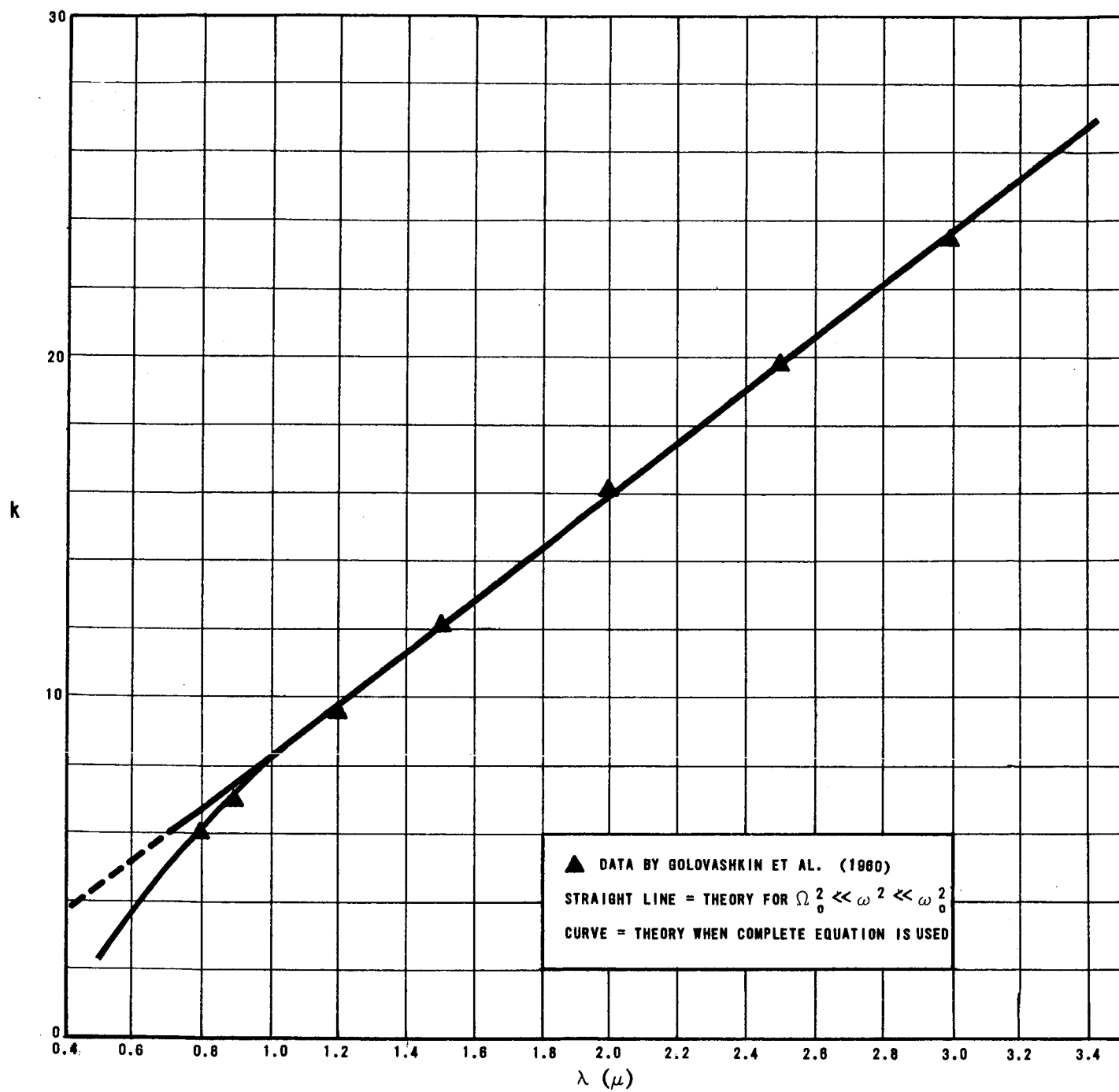


FIGURE 17

Aluminum (78°K) k vs λ

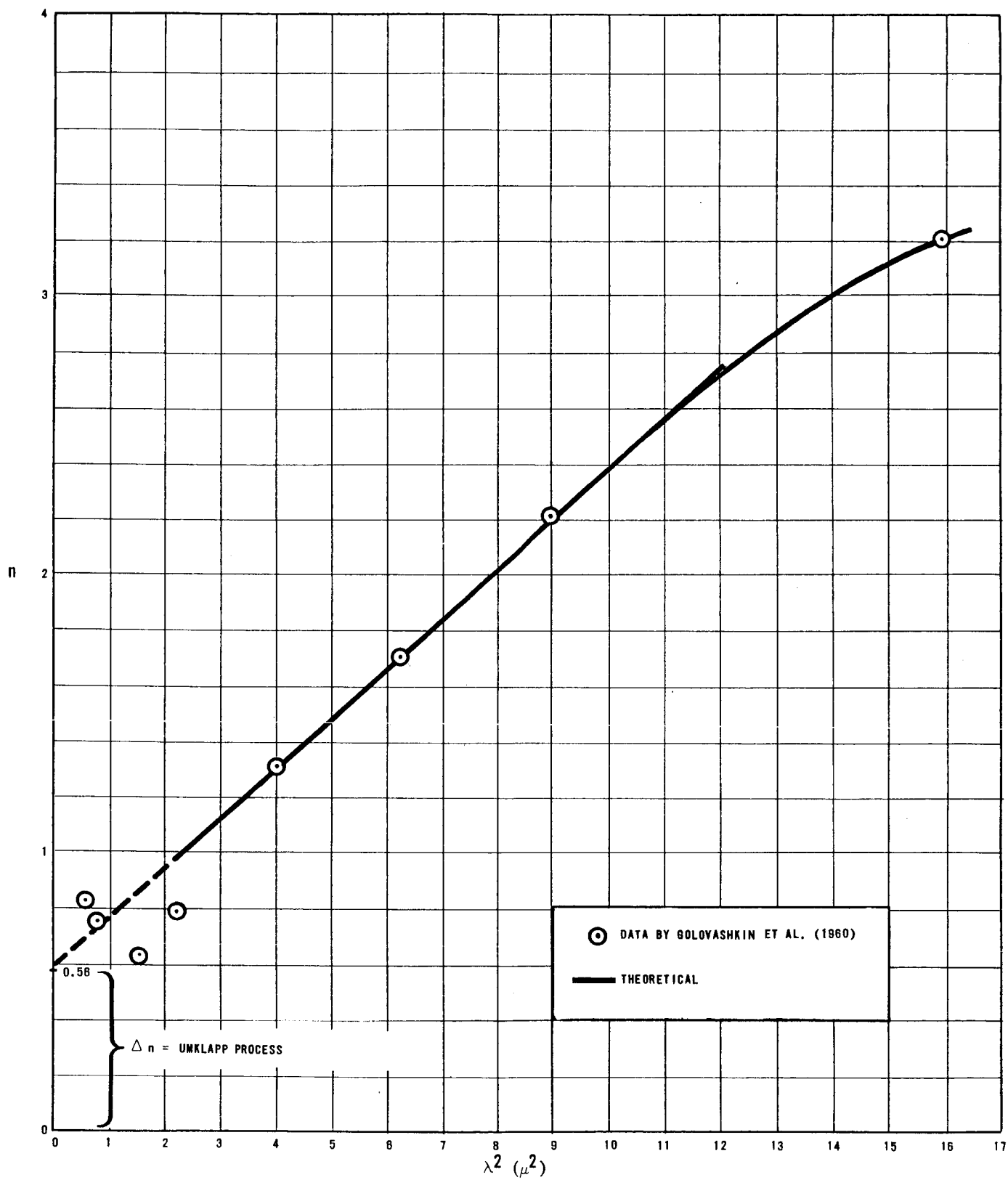


FIGURE 18

Aluminum (78°K) n vs λ^2

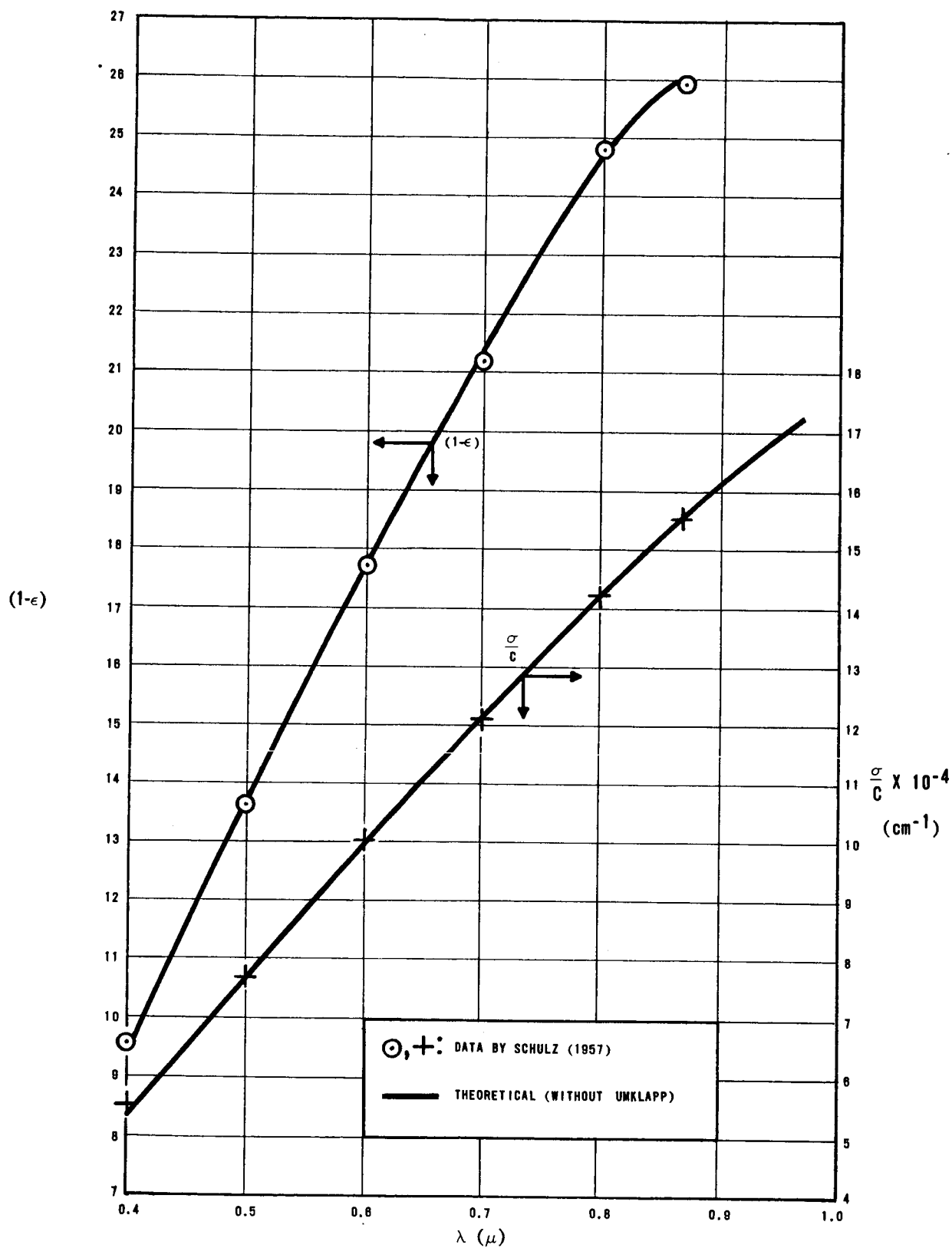


FIGURE 19

Mercury ($\sim 300^\circ\text{K}$) $(1-\epsilon)$ and $\frac{\sigma}{C}$
vs λ

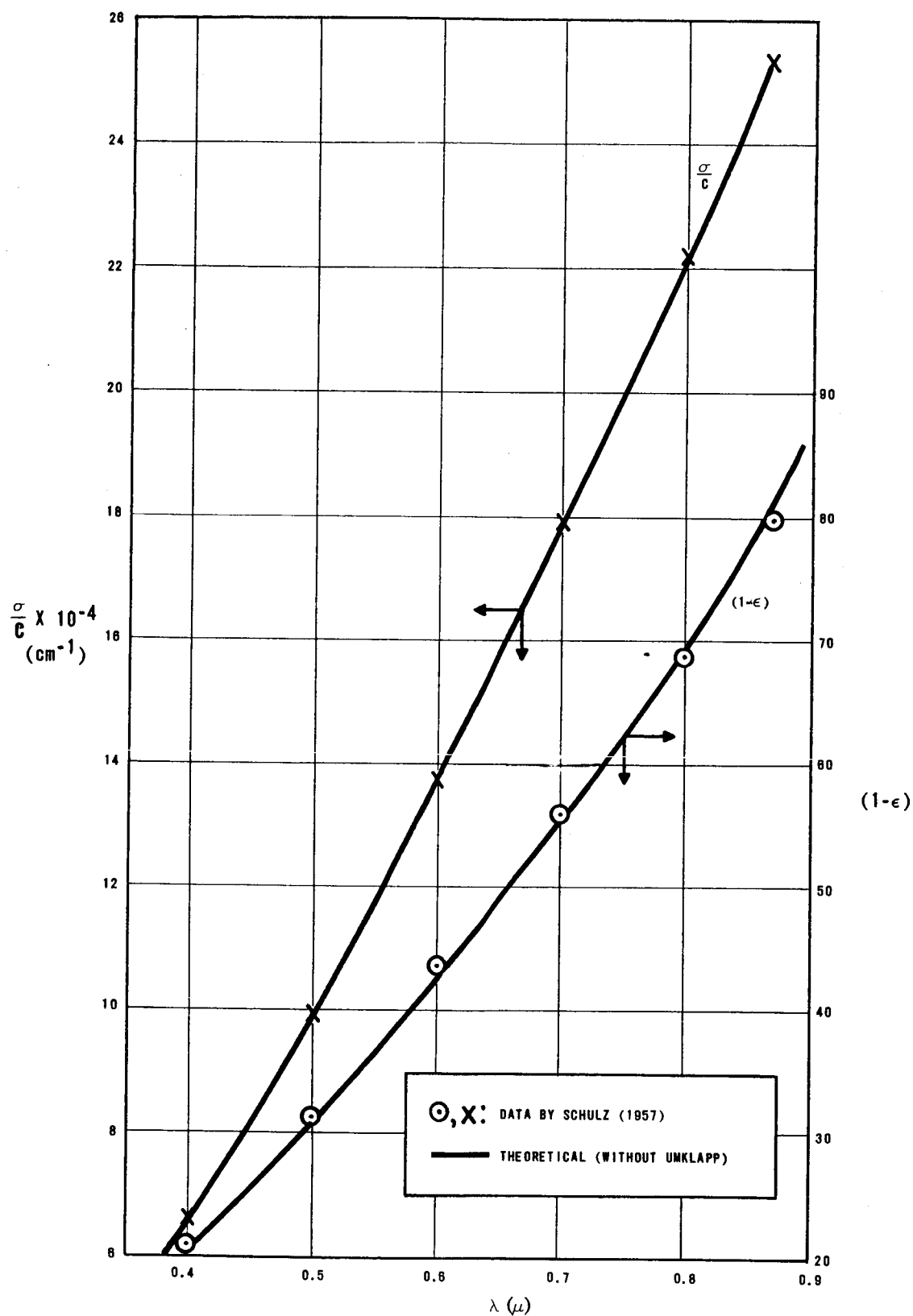


FIGURE 20

Gallium ($\sim 300^\circ\text{K}$)

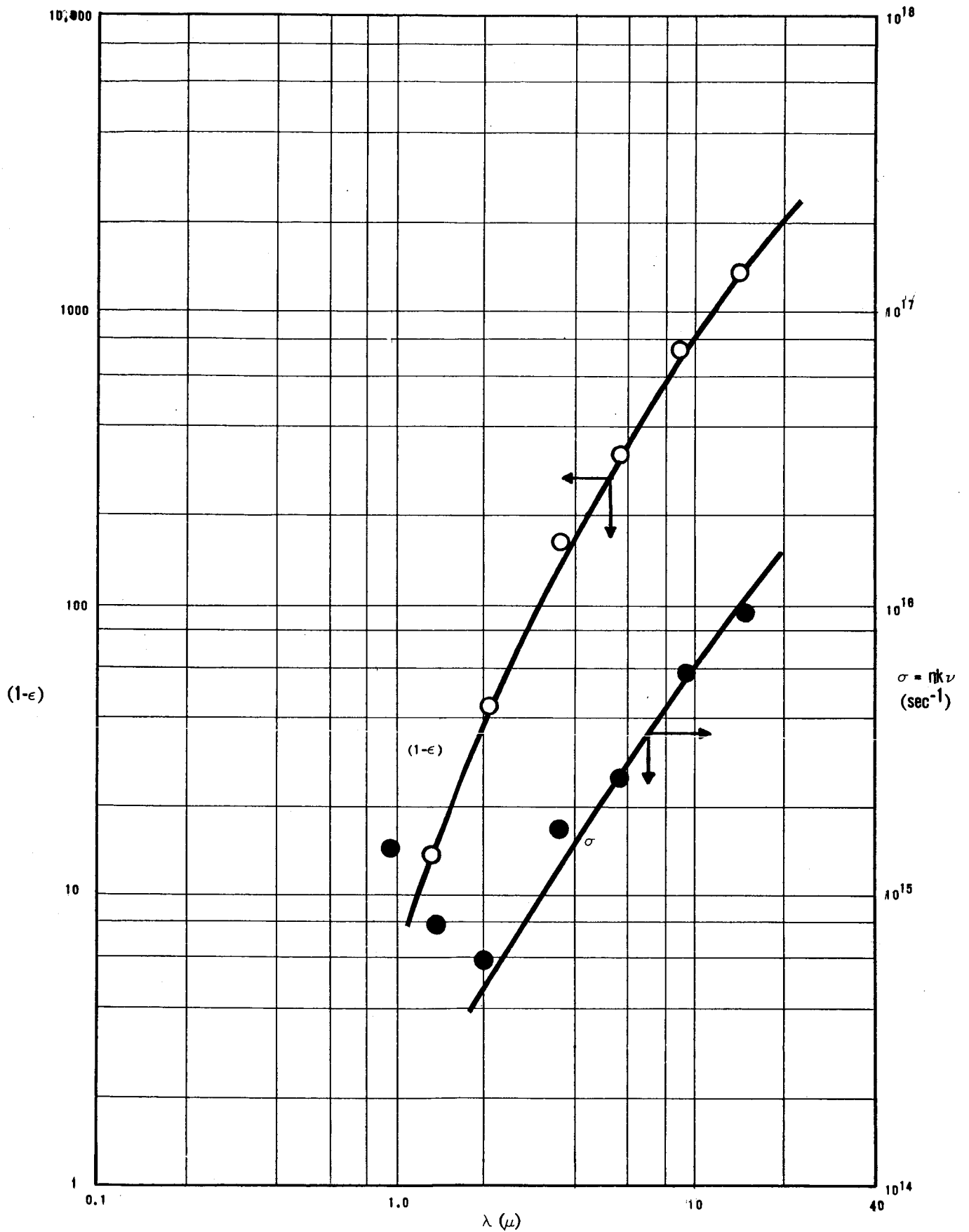


FIGURE 21

Zinc (without Umklapp)

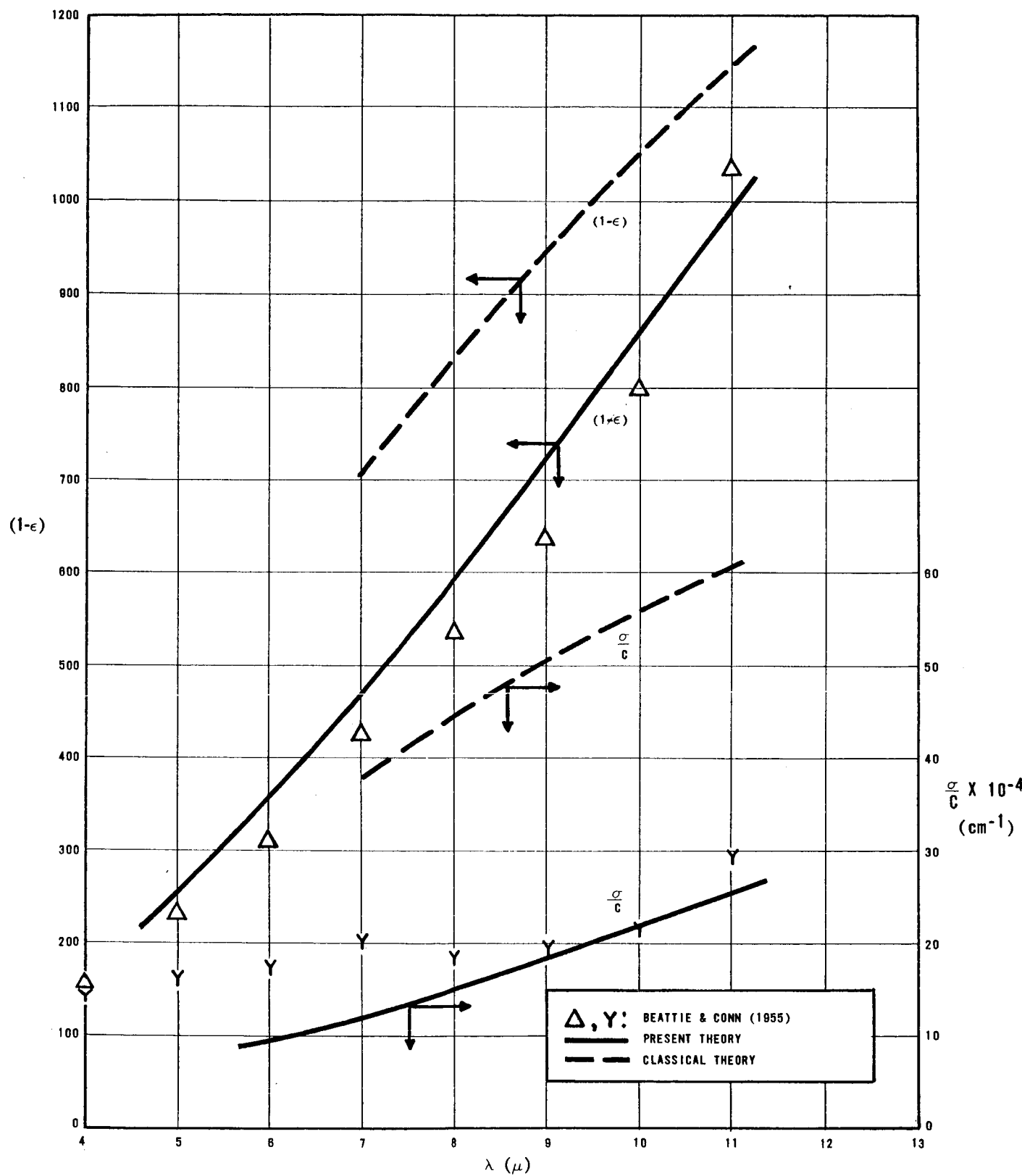


FIGURE 22

Nickel ($\sim 300^\circ\text{K}$)

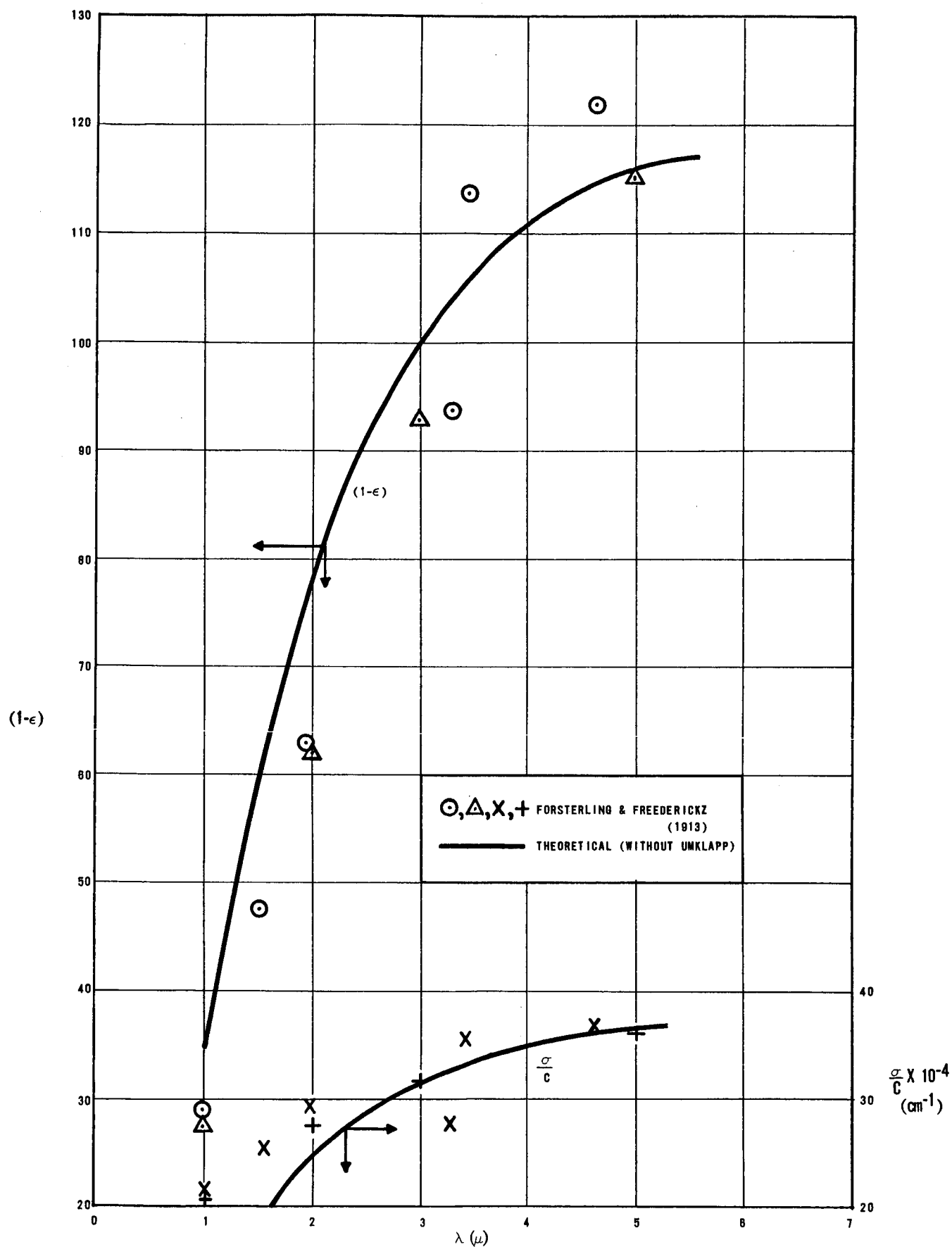


FIGURE 23

Platinum ($\sim 300^\circ\text{K}$)

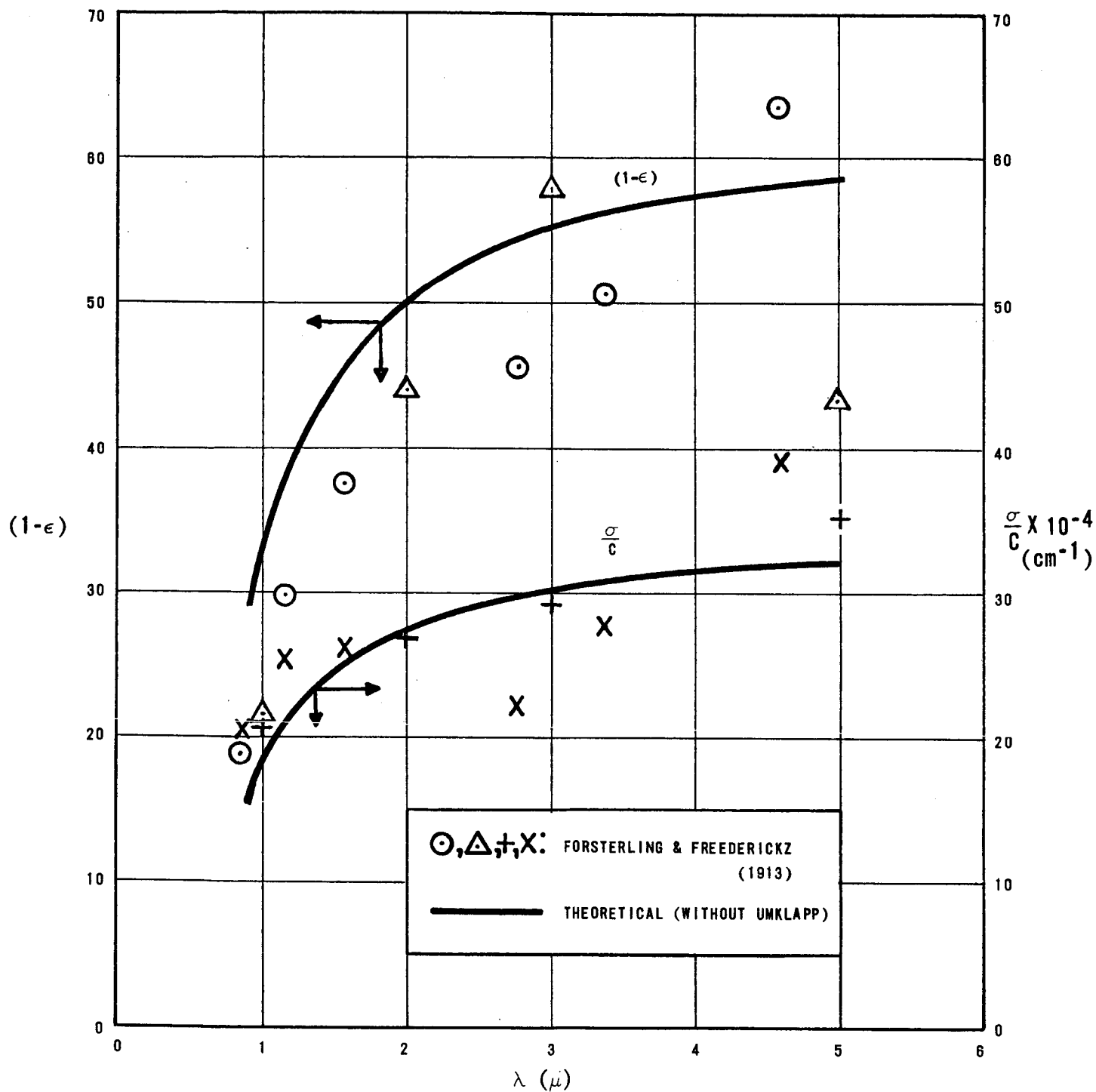
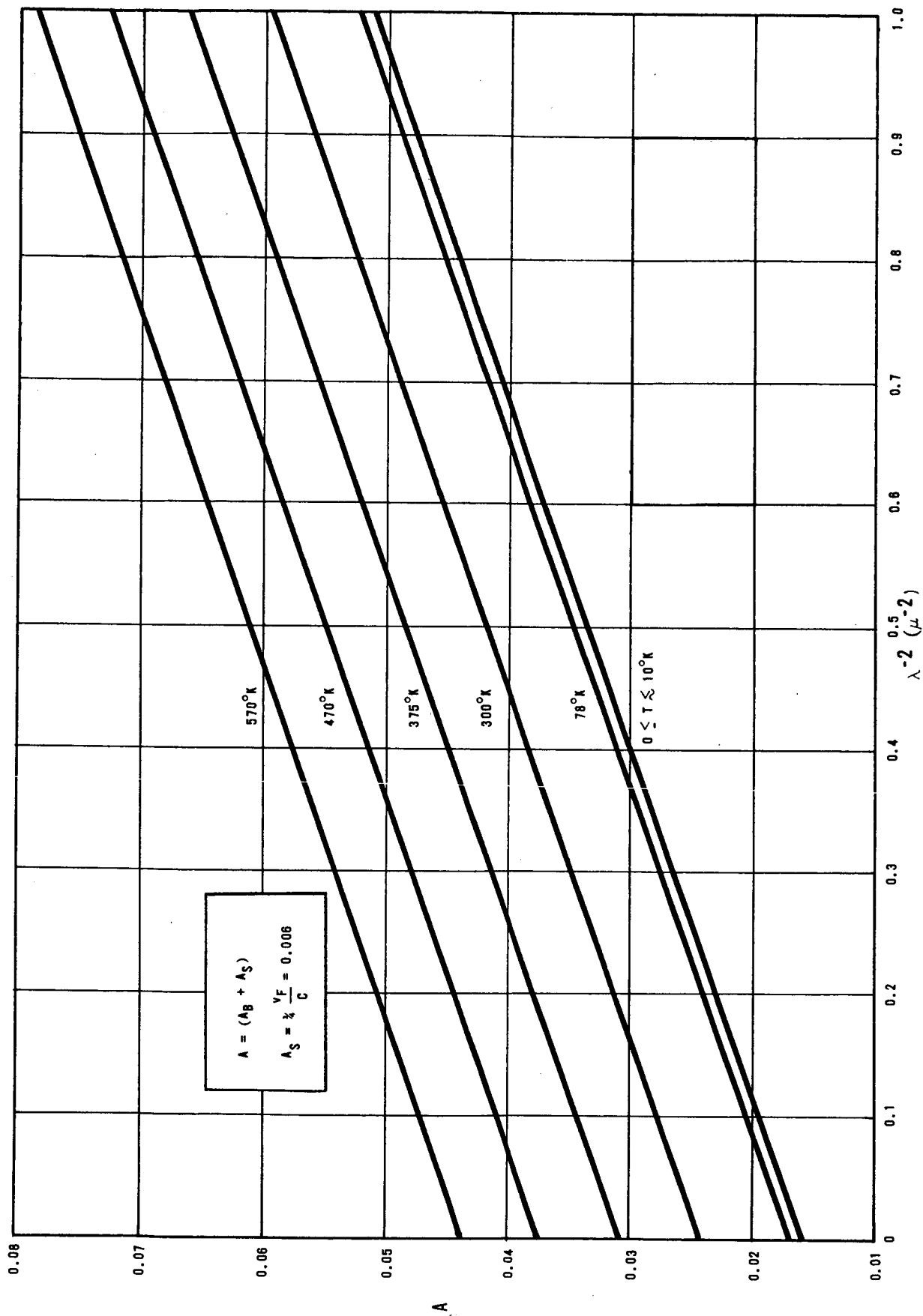


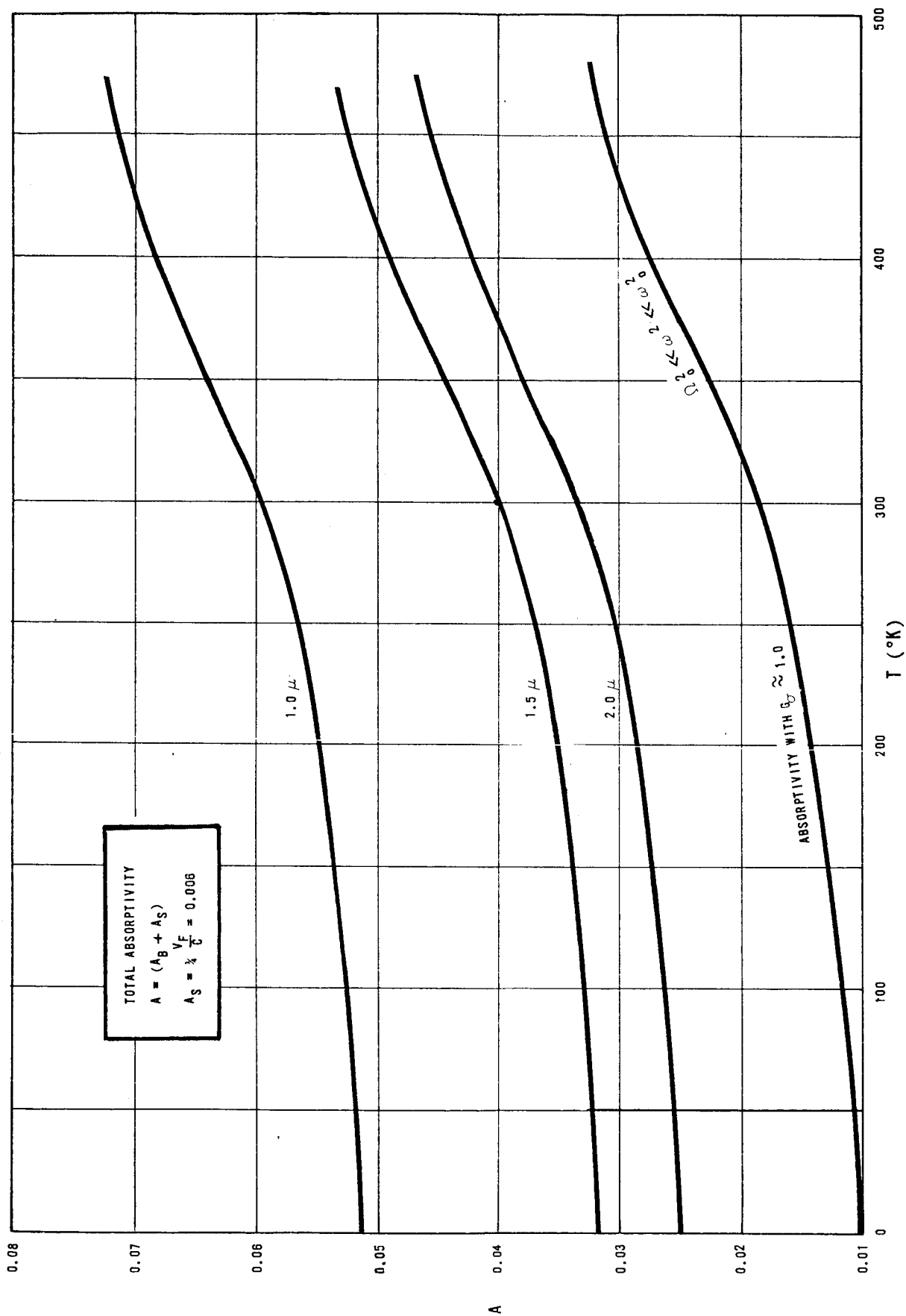
FIGURE 24

Iridium ($\sim 300^\circ\text{K}$) $(1-\epsilon)$ and $\frac{\sigma}{c}$ vs λ



Aluminum -- Total Absorptivity, A , vs λ^{-2}

FIGURE 25



Aluminum

FIGURE 26

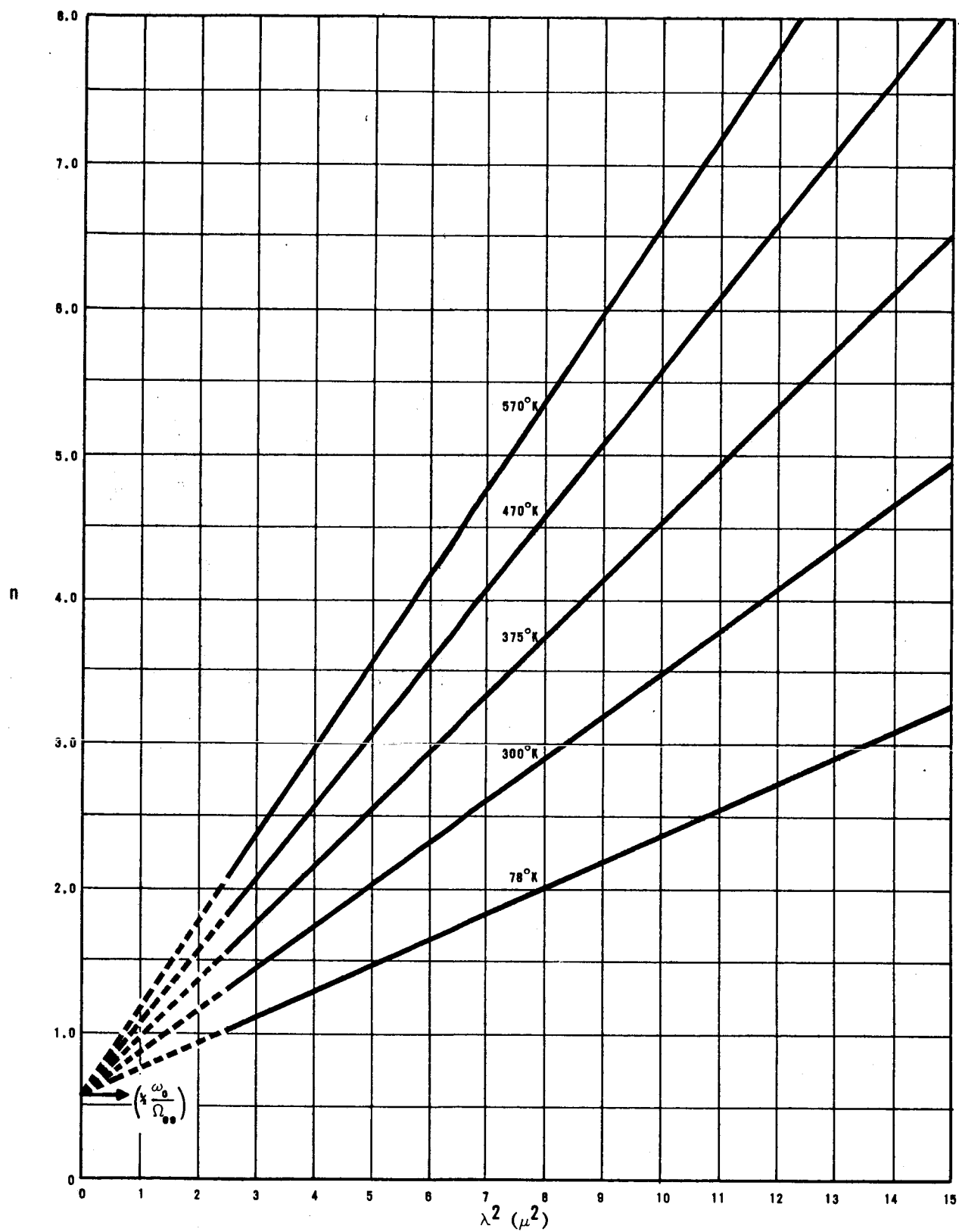


FIGURE 27

Aluminum n vs λ^2 (Theoretical values at different temperatures)

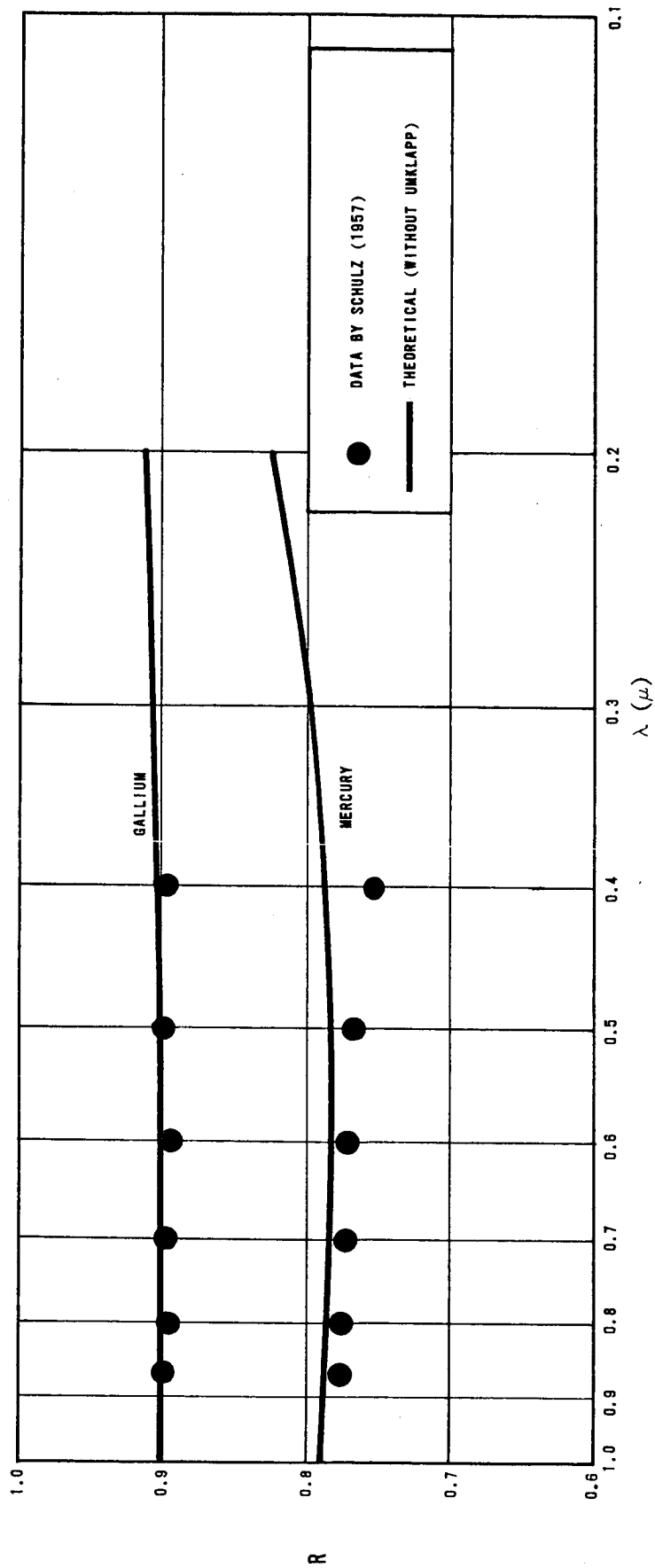
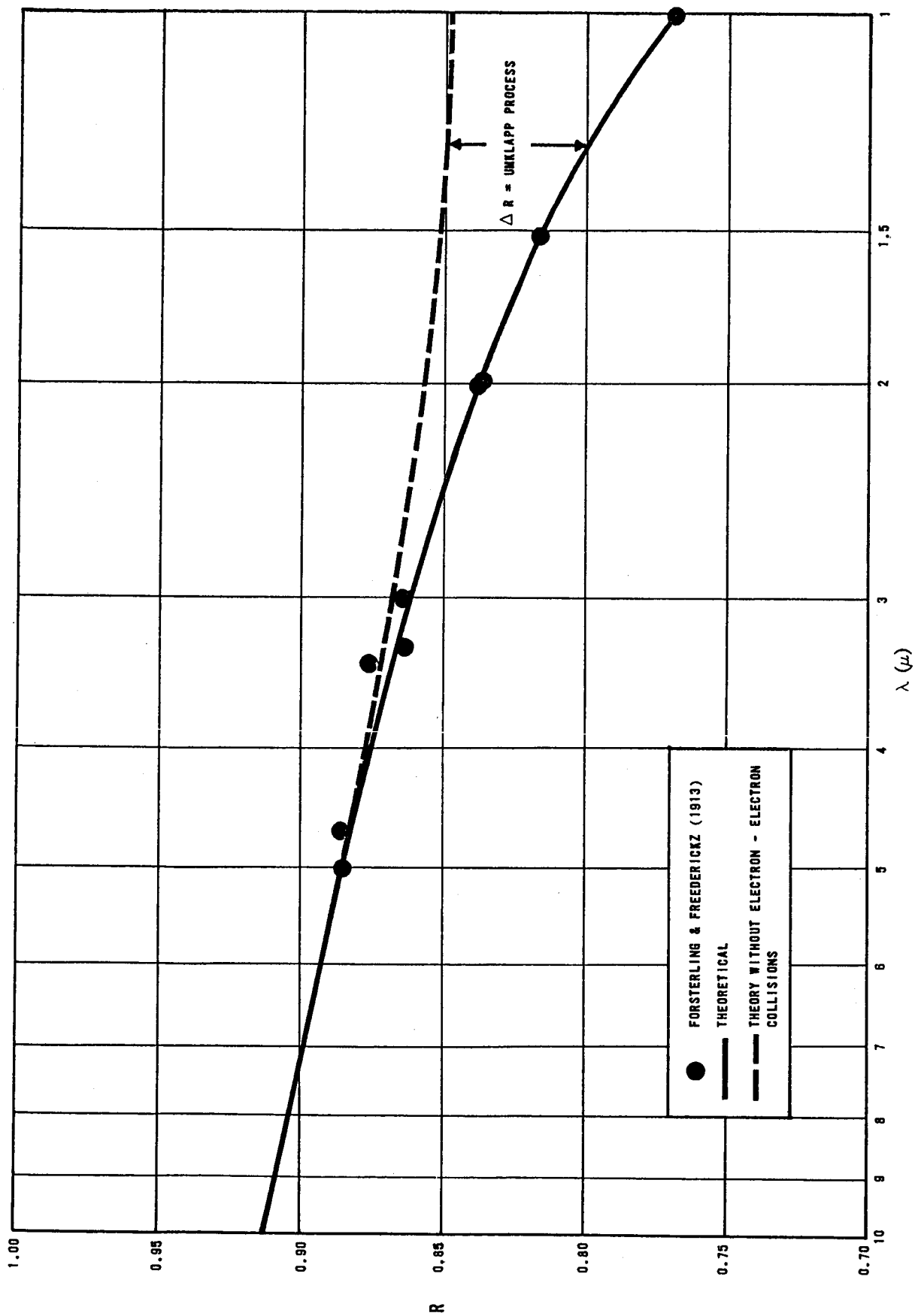
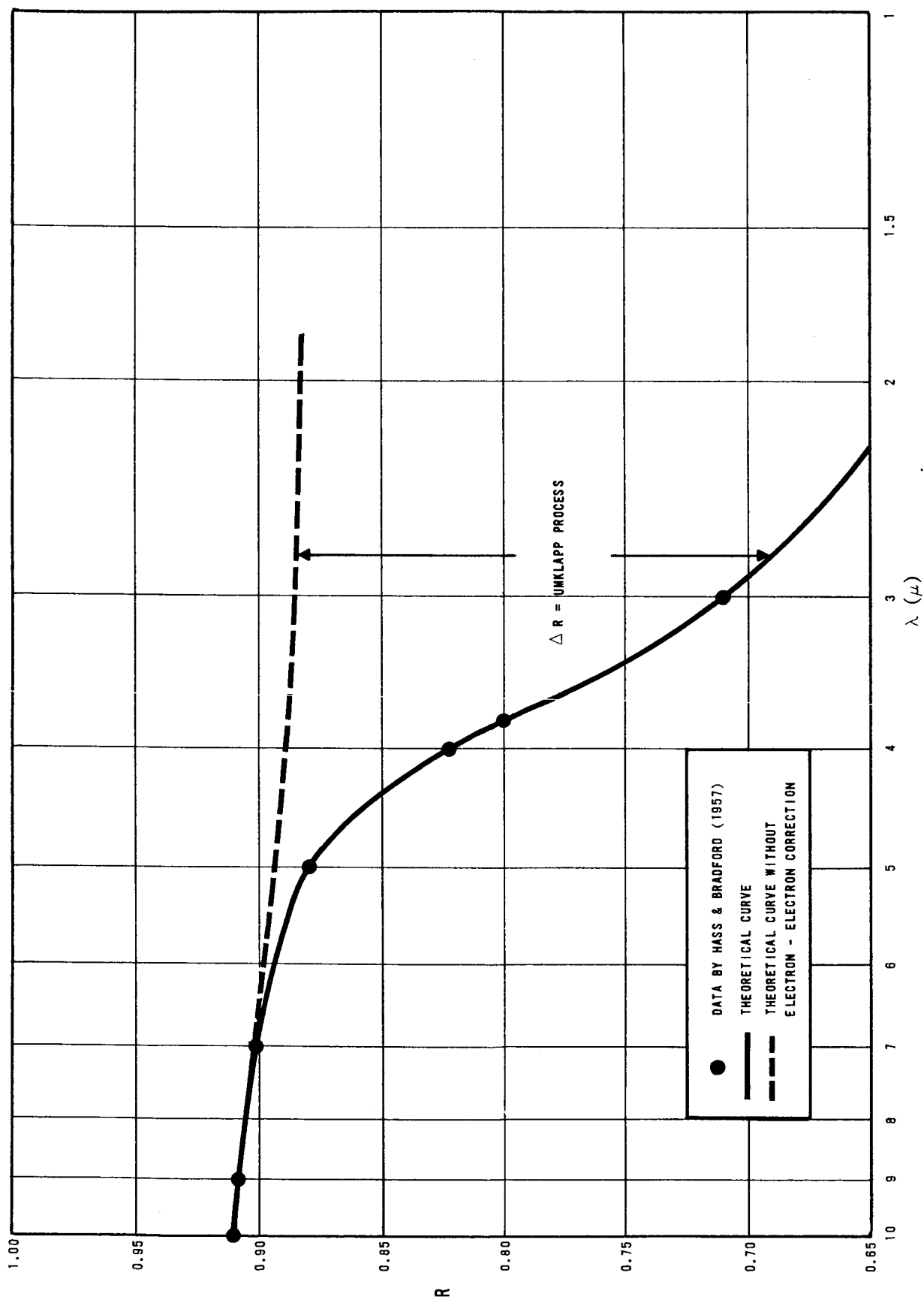


FIGURE 28 Reflectivity of Mercury and Gallium (300 °K)



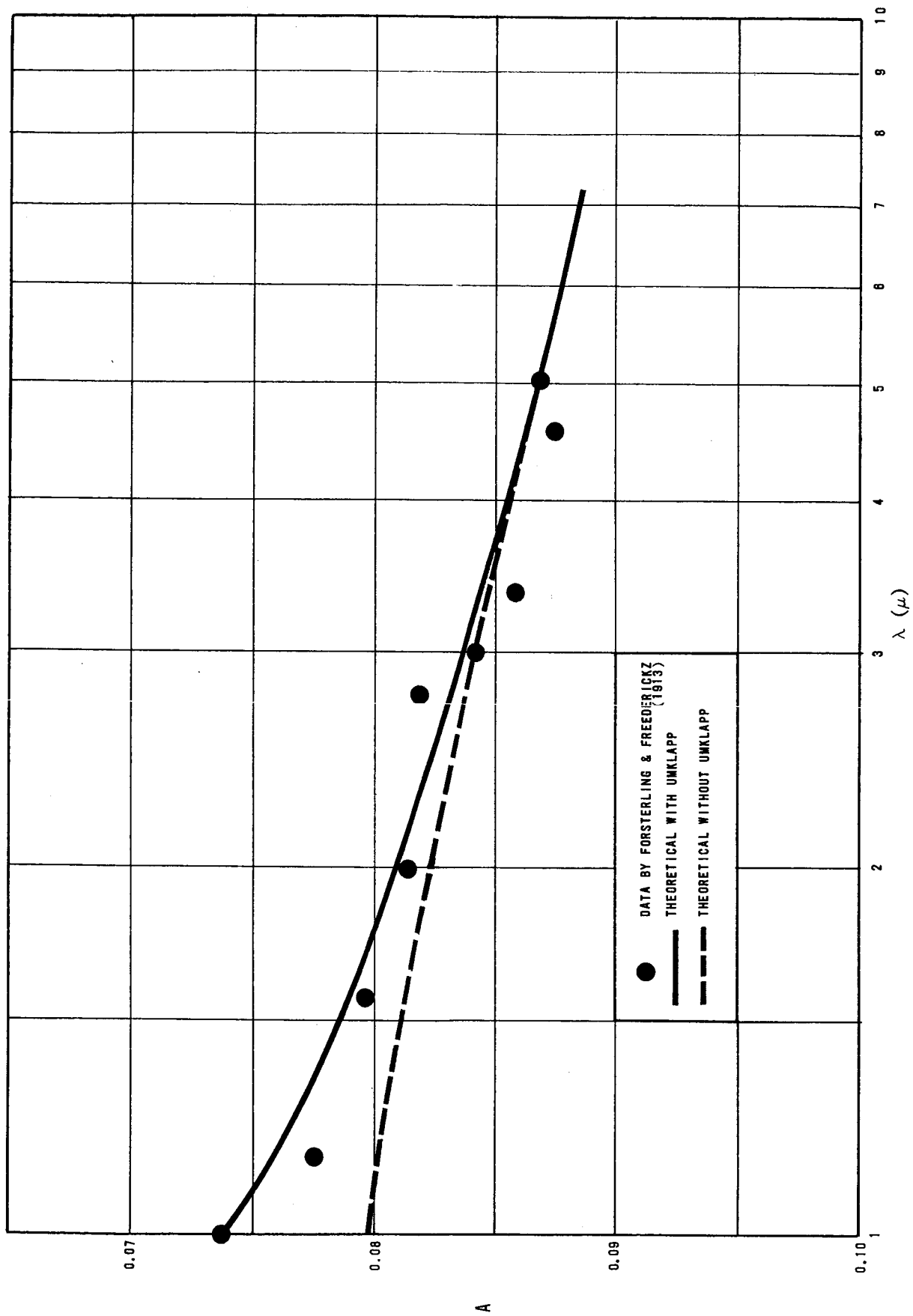
Platinum ($\sim 300^\circ\text{K}$) Reflectivity vs λ

FIGURE 29



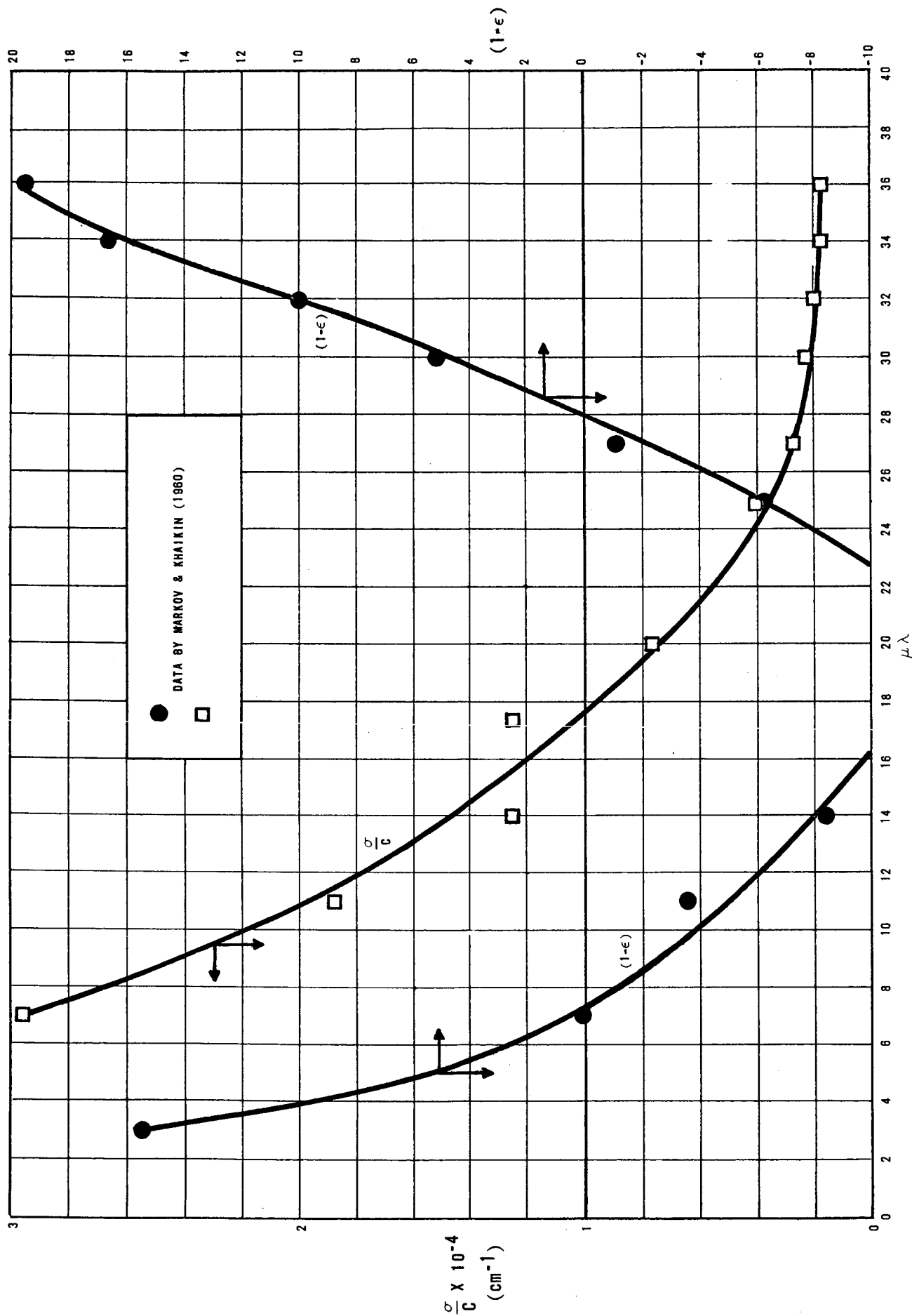
Titanium ($\sim 300^\circ\text{K}$)

FIGURE 30



Tridium ($\sim 300^{\circ}\text{K}$) Absorptivity vs λ

FIGURE 31



Bismuth ($\sim 300^\circ\text{K}$)

FIGURE 32

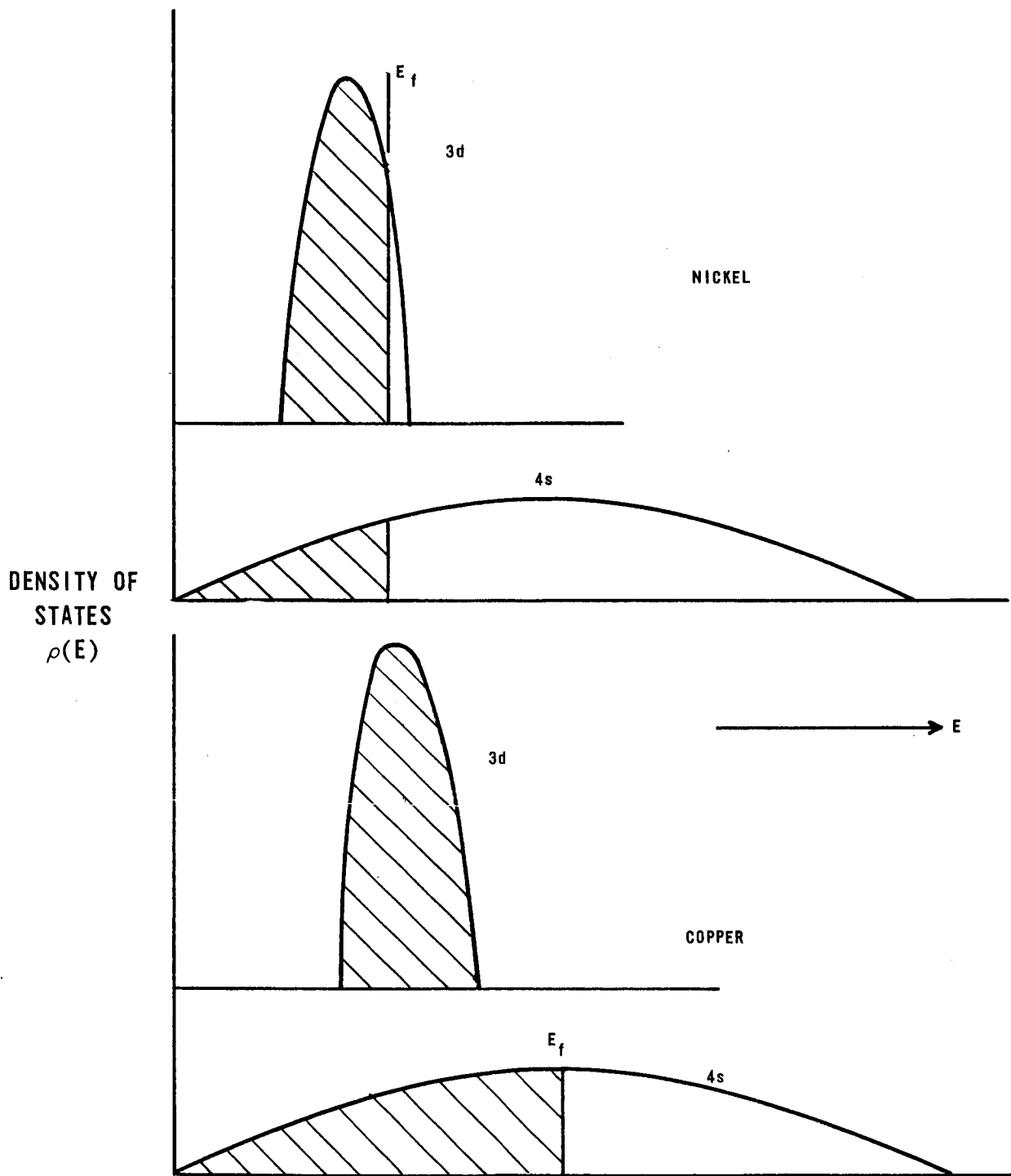


FIGURE 33

The Density-of-States Functions of Nickel at 3d-and 4s-States Compared with Those of Copper

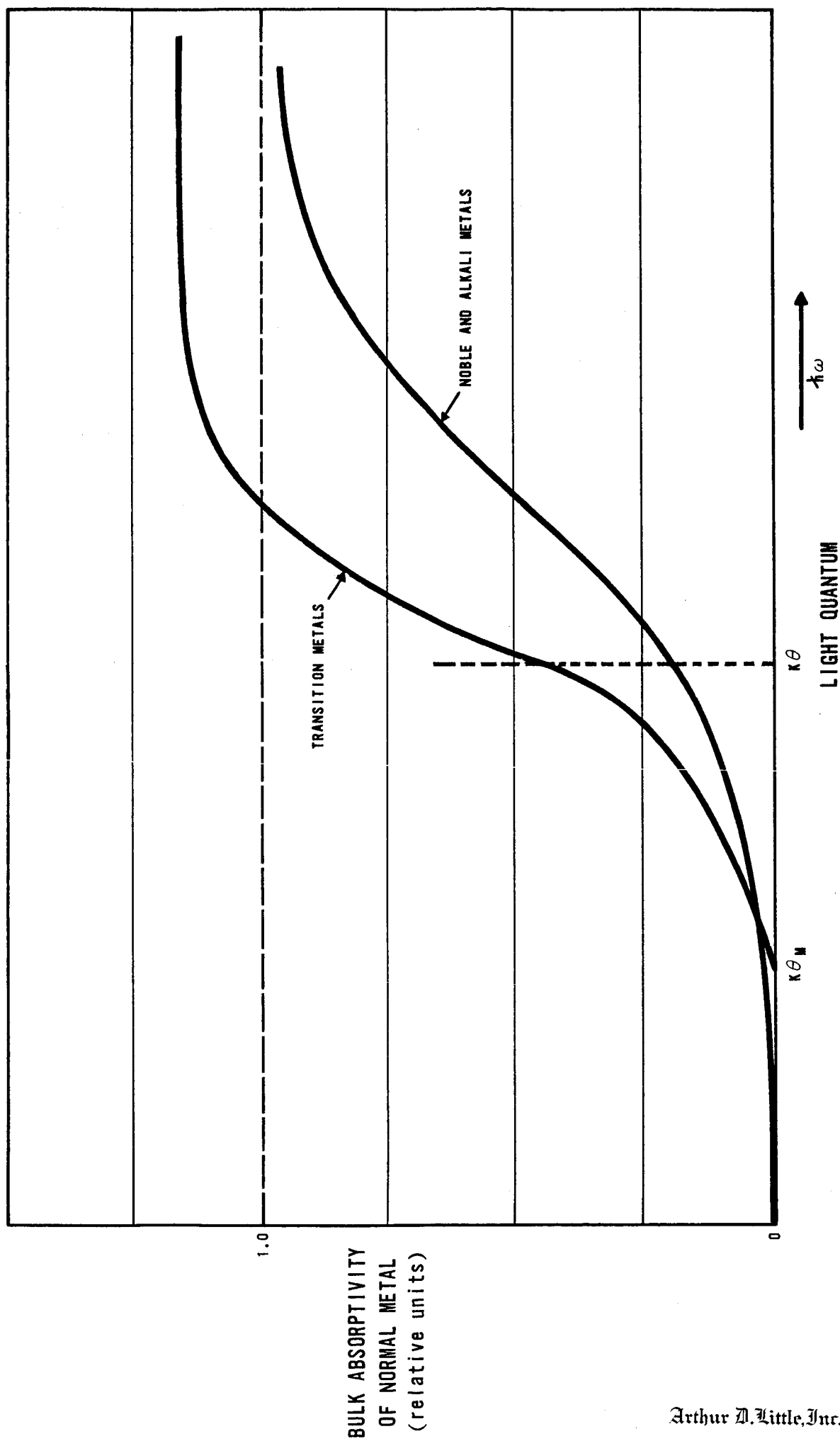


FIGURE 34 Bulk Absorptivity of Normal Metal at $T \approx 0^\circ\text{K}$

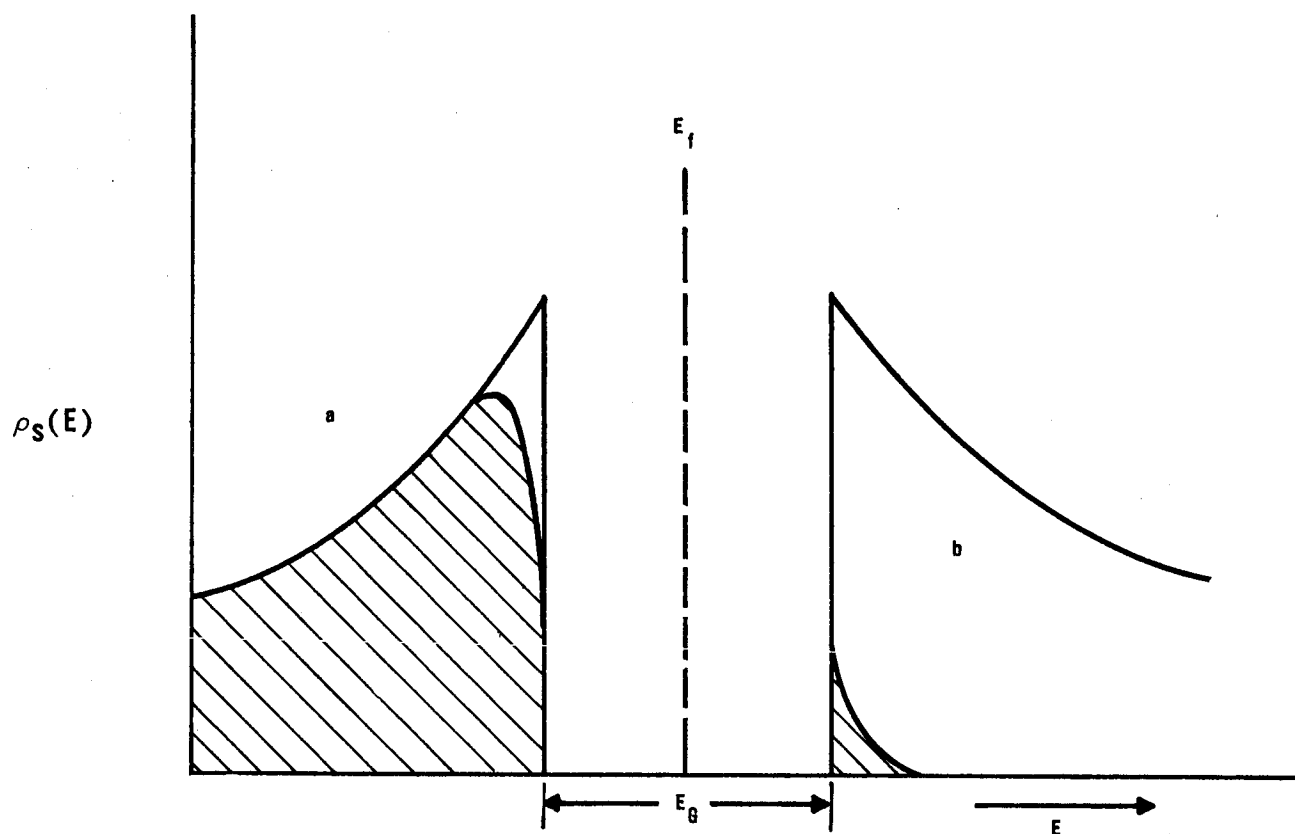


FIGURE 35

The BCS Density-of-States Function for Superconductor

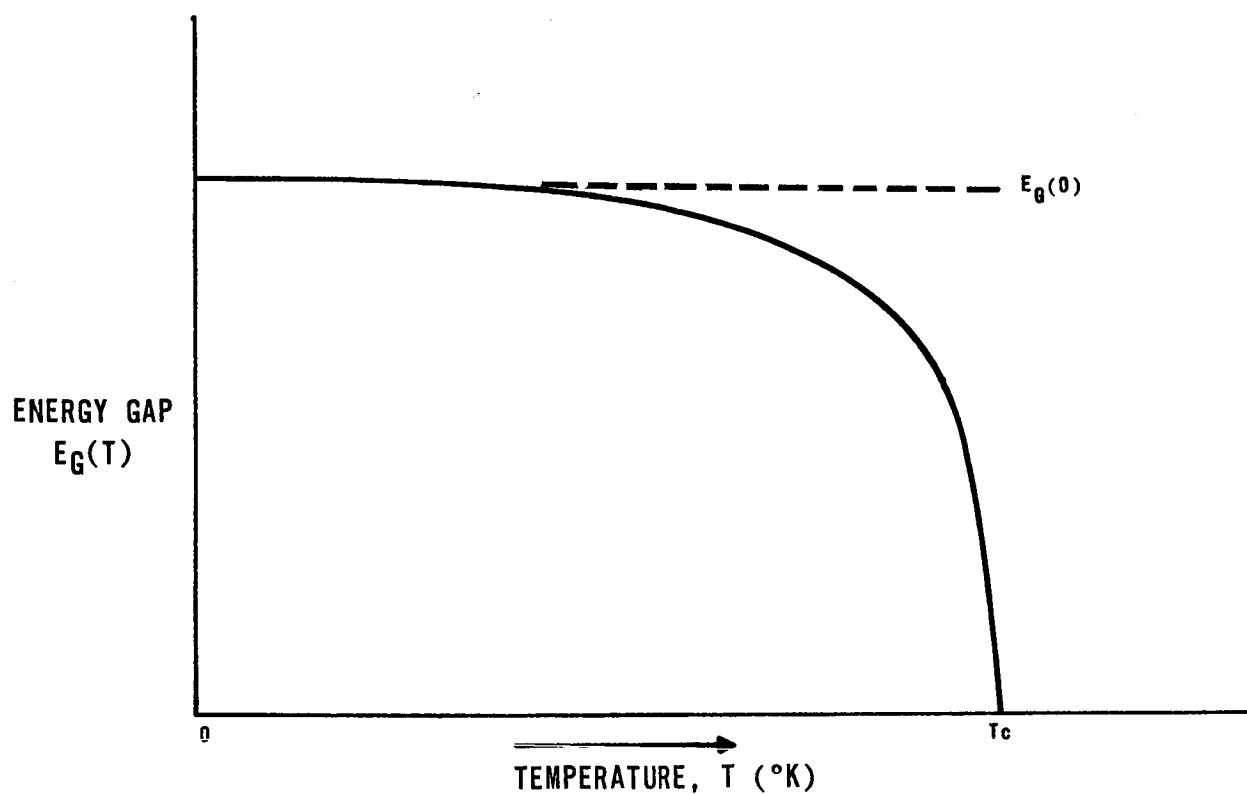


FIGURE 36

The Superconducting Energy Gap vs
Temperature

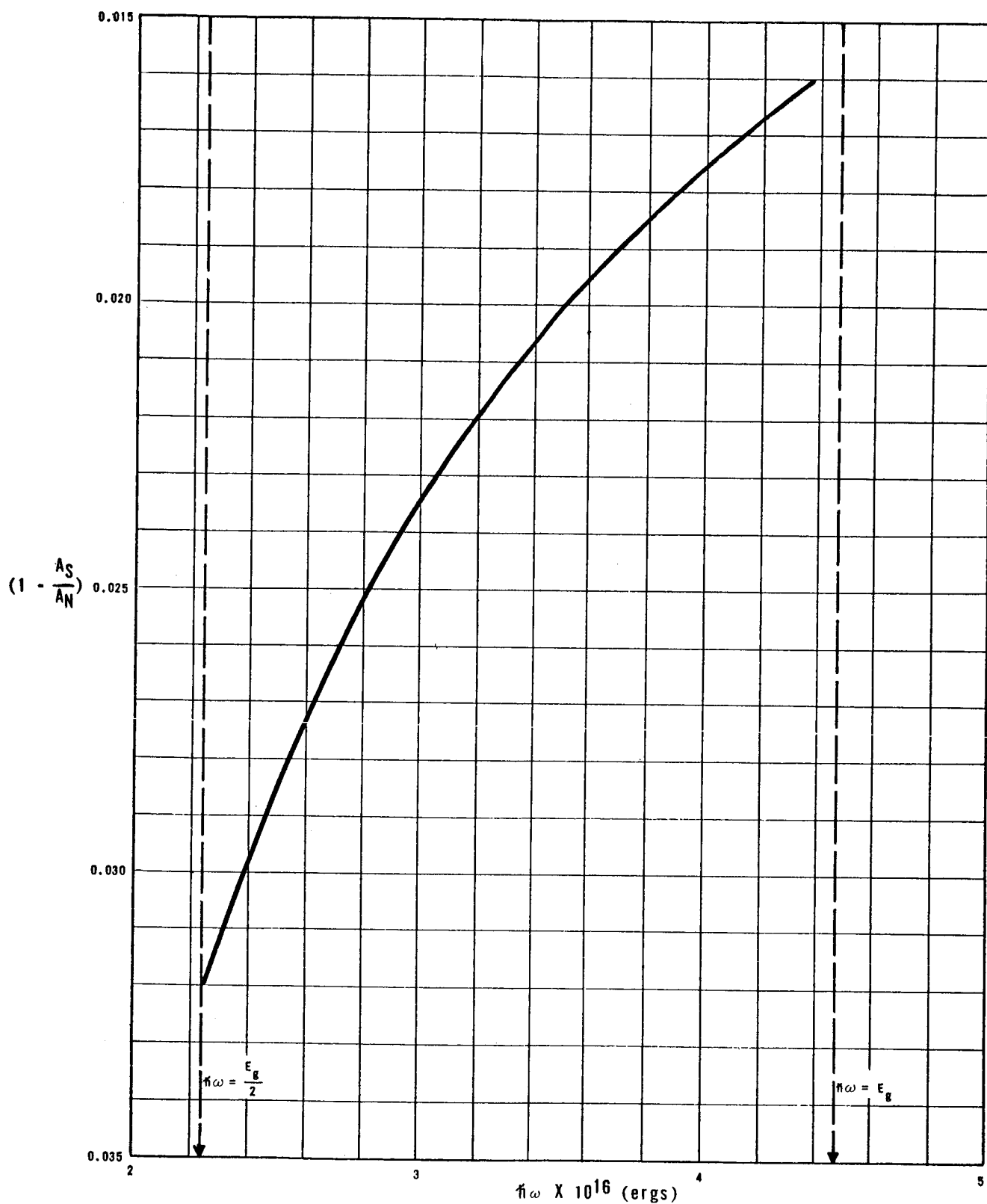


FIGURE 37

Absorptivity of Superconducting Aluminum
for $\frac{E_g}{2} < \hbar\omega < E_g$ from Formula by Schrieffer
(1960)

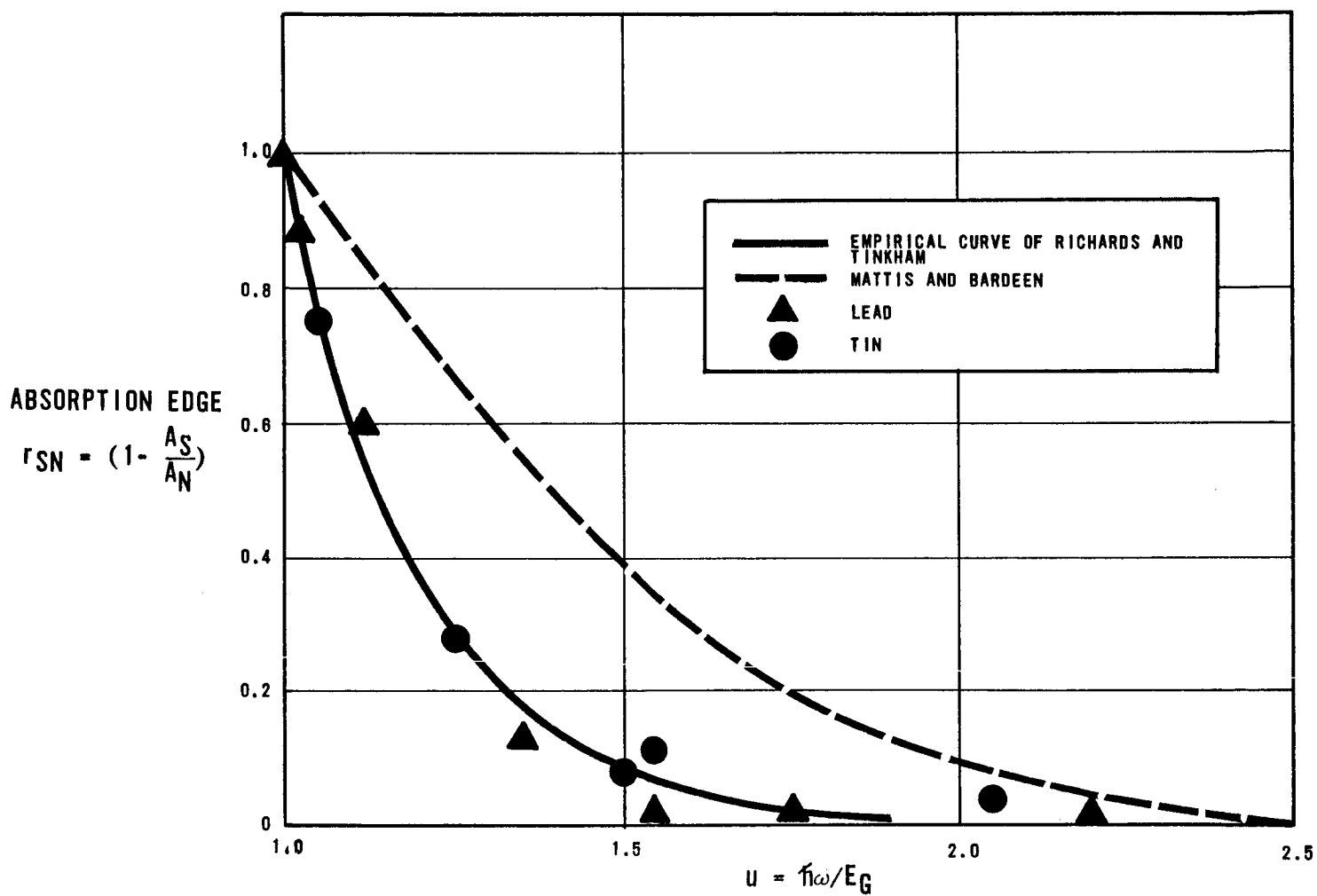


FIGURE 38

The Absorption Edge of Superconducting Tin and Lead

Chapter VII

Theory Applied to Optical Data

VII-A Calculation of Microscopic Parameters

The microscopic parameters that define the optical dispersion properties may be calculated from the best-fit theoretical curves of either the optical constants (n, k) or (σ, ϵ) . In general, it is much simpler to use the data on (σ, ϵ) rather than (n, k) since the general formulae for the former are less complicated than the latter. If the optical data are available in the spectral range, $\tilde{\nu}_0^2 \tilde{\nu}_\infty^2 \ll \omega^2 \ll \omega_0^2$, which, for many metals, corresponds to $1\mu \lesssim \lambda < 10\mu$, it is convenient to use the best-fit theoretical curves of (n, k) . In this part of the spectrum, the theoretical formula for k is exactly the same as that given by the classical Drude theory while the formula for n can differ substantially from the classical formula; namely,

$$k \cong \left(\frac{\omega_0}{\omega} \right) = \left(\frac{\lambda}{\lambda_0} \right) \quad \text{VII-(1)}$$

$$n \cong \frac{i}{2} \frac{\omega_0 \tilde{\nu}_\infty}{\omega^2} \tilde{G}_\sigma$$

$$= 1/2 \left[\frac{\omega_o \tilde{\Omega}_o}{\omega^2} + \frac{\omega_o}{\Omega_{ee}} \right]$$

VII-(2)

$$\tilde{\Omega}_o = \left(\Gamma_{ep}^o \tilde{b}_{ep} + \Gamma_{ee}^o + \Gamma_M^o \right)$$

It is seen that k describes a straight line when it is plotted against λ while n describes a straight line when it is plotted against λ^2 . The critical frequency ω_o is obtained from (1), and when this is used in (2), the numerical values of $\tilde{\Omega}_o$ and Ω_{ee} follow immediately. The value of the electron-electron damping coefficient Γ_{ee}^o is obtained from Ω_{ee} when we use the relation,

$$\Omega_{ee} = \left(\frac{\hbar \beta}{2\pi} \right)^2 \Gamma_{ee}^o = \left(\frac{\hbar \beta_o}{2\pi} \right)^2 R_{ee}$$

$$\beta = 1/KT$$

VII-3

$$\beta_o = 1/K\theta$$

where R_{ee} is a constant which is independent of ω and T . The values of Γ_{ep}^o and hence R_{ep} can be determined from (1) and (2) only when we neglect Γ_M^o compared with Γ_{ee}^o and Γ_{ep}^o . This procedure is valid for metals which are substantially free of impurities, provided that the temperature is not too low. The method of determining the "Restwiderstand" term, Γ_M^o

from the low-temperature optical data will be explained in a later part of this chapter.

Once the values of ω_0 , R_{ep} , and R_{ee} are determined, we can predict the values of (n,k) and other dispersion quantities at any other temperature and frequency.

It is important to note that, in fitting (1) to the corresponding experimental curve, the extrapolated straight line must pass through the origin at $\lambda = 0$, and that, when (2) is plotted against λ^2 , the non-zero value of n defined by the intersection of the straight line at $\lambda = 0$ is entirely due to the Umklapp processes which give rise to a non-zero contribution of the electron-electron collisions.

The remarkable qualities of the formulae (1) and (2) are clearly demonstrated in Figure 8 to 11 for gold and copper, and in Figures 15 to 18 for the multivalent aluminum.

For many metals, it is not easy to identify the portion of the spectrum where the formulae (1) and (2) are applicable, and the general formulae of chapter V need be used. In this case, it is more convenient to obtain the best-fit theoretical curves of (σ, ϵ) than of (n,k) using the formulae;

$$\sigma = \frac{\omega_0^2}{4\pi} \tilde{n}_0 \tilde{G}_\sigma / (\omega^2 + \tilde{n}_0^2)$$

$$[1 - \epsilon] = \omega_0^2 / (\omega^2 + \tilde{n}_0^2) \quad \text{VII-(4)}$$

where \tilde{N}_0 and \bar{N}_0 are independent of ω .

The best-fit theoretical curves of σ and $[1 - \epsilon]$ are shown in Figure 7, Figure 12-14, and Figures 19-24 for ten different metals including the noble, multivalent, and transition metals. In particular, the multivalent metal, aluminum, is examined at two different temperatures, 78° K. and 295° K.

Table IX shows the numerical values of various microscopic parameters that are calculated from Figure 7-24. These parameters are sufficient to enable us to calculate the d.c. electric properties and the dispersion properties at different spectral and temperature ranges.

The d.c. electrical conductivity σ_0 is calculated from the formulae,

$$\sigma_0 = \frac{\omega_0^2}{4\pi} \frac{1}{\Gamma^0}$$

$$\Gamma^0 = \Gamma_{ep}^0 + \Gamma_{ee}^0 + \Gamma_M^0$$

VII-(5)

where Γ_M^0 may be ignored at ordinary temperature. The theoretical and measured values of σ_0 are shown in Table VII for a variety of metals. For most of the metals that are examined, the theoretically calculated values agree well with the electrically measured values. Note, in particular, that

the values for N_i and A have been improved considerably from the old values of Table I. In Table VII, some of the measured values of σ_o are not obtained from the samples on which the optical data are available. For an accurate comparison between the calculated and measured values of σ_o , both the optical and electrical measurements must be made on the same sample, since, as was explained in Chapter III, the optical and electric properties vary depending on the manner in which the metallic surface is prepared. For instance, most of the available optical data are obtained from vacuum evaporated surfaces while the handbook values of σ_o are for bulk samples. Beattie and Conn (1955) obtained the optical data for several metals, each with several different surface preparations. The variation in the values of the electrical and optical properties among differently prepared metal surfaces was quite substantial.

VII-B Calculation of Absorptivity

With the help of the microscopic parameters that are given in Table IX, the absorptivity is calculated from the formula,

$$A_B \approx \frac{2}{\omega_o} \kappa_o G_\sigma \left[1 - \frac{9}{8} \left(\frac{\kappa_o}{\omega} \right)^2 + \frac{37}{32} \left(\frac{\kappa_o}{\omega} \right)^4 + \dots \right] : \omega > \kappa_o > \bar{\kappa}_o$$

$$A_S = \frac{3}{4} \frac{v_F}{c}$$

$$A = A_B + A_S$$

VII-(6)

where A_s is the absorptivity due to the diffuse surface scattering (Dingle, 1953). The skin absorption is important when the mean free path given by

$$\ell = v_F \tau_R \quad \text{VII-(7)}$$

is much larger than the skin depth δ_s which was given in Chapter III, where τ_R , unlike the d.c. relaxation time τ_R^o , is now given by

$$\frac{1}{\tau_R} = \frac{1}{\tau_R^o} + \Gamma_{ep}^o (\tilde{b}_{ep} - 1) \quad \text{VII-(8)}$$

According to the original theory of the anomalous skin effect, the d.c. relaxation time τ_R^o was used in Equation (7) so that, at low temperatures, ℓ can be substantially larger than δ_s due to the rapid decrease of Γ^o with decrease in temperature.

According to the present theory, however, τ_R does not increase so fast as might have been expected from the theory of electric conduction, since a rapid increase of \tilde{b}_{ep} according to $\sim \left(\frac{\Theta}{T}\right)^5 \frac{1}{J_F^o}$ completely counteracts the rapid decrease of Γ_{ep}^o , until τ_R reaches the constant low-temperature value,

$$\frac{1}{\tau_R} \approx \left(\frac{1}{10} R_{ep} + \Gamma_M^{\circ} \right) : T \approx 0^{\circ}K$$

VII-9

This is to be compared with

$$\frac{1}{\tau_R^{\circ}} \approx \Gamma_M^{\circ} : T \approx 0^{\circ}K$$

VII-(10)

which results when Γ_{ep}° is used in place of Γ° .

As the result of this, the absorption due to the anomalous skin effects is not so significant in the present theory as was suggested in the original theories of Reuter and Sondheimer (1948) and Dingle (1953). For transition metals and also for multivalent metals for which inter-band transitions are predominant, the relation (9) is replaced by

$$\frac{1}{\tau_R} \approx \left(\frac{R_{ep}^{s \rightarrow d}}{6} + \Gamma_M^{\circ} \right)$$

VII-(11)

The constant R_{ep} can be obtained from the known values of Γ_{ep}° upon using the relation,

$$\Gamma_{ep}^{\circ} = R_{ep} \frac{1}{\alpha^5} J_5^{\circ}(\alpha)$$

VII-(12)

for nontransition metals, and the relation

$$\Gamma_{ep}^o = R_{ep}^{sd} \frac{1}{\alpha^3} J_3^o(\alpha) \quad \text{VII-(13)}$$

for transition metals, where the functions J_5^o and J_3^o are available in the appendix in calculable forms: the numerical values of $J_5^o(\alpha)$ are computed in Table V and VI. Since R_{ep} is usually $\frac{1}{10} \sim 1$ times as large as Γ_{ep}^o at room temperature, τ_R for both transition and non-transition metals at very low temperatures and in the near infrared is given by

$$\tau_R \approx (10 \sim 10^2) \times \tau_R^o(300^\circ K) \quad \text{VII-(14)}$$

which implies that the mean free path l increases by a factor of $10 \sim 100$ when T is lowered from room temperature to the absolute zero. This is in marked contrast to the low-temperature electrical properties and also to the existing theories of optical dispersion.

The absorptivity values that are computed from (6) are presented in Figure 28-31 and are compared with the experimental curves for the liquid metals, Hg and Ga, and for the transition metals, Pt, Ti, and Ir. The contributions by the Umklapp processes are indicated in Figures 29-31. One glance at these curves is sufficient to show that the transition metals with

predominantly interband transitions exhibit a markedly greater contributions of the Umklapp processes than other metals.

Table II shows the theoretical values of the low-temperature (4.2°K) and near infrared ($1\sim 2\mu$) absorptivity of eleven different metals. The theoretical values for Cu and Ag are in agreement with the experimental values of Biondi (1956) within $\sim 2\%$. Unfortunately, the experimental values are as yet unavailable on other metals, and no further comparison is possible. The relative importance of the bulk absorption as compared with the skin absorption is represented by computing the per cent value of $\left(\frac{A_B}{A}\right) = \left(1 - \frac{A_S}{A}\right)$.

It is seen that for all the metals that are studied, the bulk absorption ranges from 20% for Ag to nearly 100% of the total absorption. In general, the bulk absorption is relatively more pronounced in multivalent and transition metals than in noble metals. It is hardly necessary to mention that, according to the classical theory, there should be almost no bulk contribution to the low-temperature absorption, and that the remarkable features demonstrated in Table II are entirely the consequence of the quantum correction factor, b_{ep} , of the present theory.

VII-(C) Calculations of Dispersion Properties at Different Temperatures

We have already demonstrated how the microscopic parameters that are computed from the room temperature optical

data can be used to compute absorptivity at very low temperatures. We may likewise calculate and hence predict the values of any dispersion property at different temperatures when the values of the fundamental microscopic parameters are available from the optical data at a particular temperature.

Before we proceed with numerical applications, we need to establish the validity of the T-dependence that is formulated in the present theory. The temperature-dependence of $\Gamma_{ee}^0(\alpha)$ is well established and has been popularly used in the past. Therefore, we need to concern ourselves only with the T-dependence of the electron-phonon damping coefficient $\Gamma_{ep}^0(\alpha)$ and the quantum-factor, $b_{ep}(\alpha, \mu)$. We explained previously that the T-dependence of $\Gamma_{ep}^0(\alpha)$ of the present theory is entirely consistent with the T-dependence of the well-known Gruneisen formula and also with that which is derived in Wilson's theory of electric conduction in metals, and that Grüneisen's formula is in excellent agreement with the observed heat capacity data: e.g. see Figure 2- (a) and -(b). Although this enables us to conclude that our formula for $\Gamma_{ep}^0(\alpha)$ is valid, we have yet to establish the validity of the T-dependence of $b_{ep}(\alpha, \mu)$ or equivalently of $\tilde{b}_{ep}(\alpha)$.

For this purpose, we shall use the optical data on aluminum which are obtained at two widely separated temperatures, 78°K and 295°K, by Golovashkin et al (1960). We saw previously

that the theoretical curves for n, k, σ and $(1-\epsilon)$ at the two temperatures agree well with the corresponding experimental curves, and that the calculated value of σ_0 at 295°K also agrees with the electrically measured value. Table IX shows further that the values of the temperature-independent parameters which are calculated from the two separate data agree with each other within $\sim 5\%$. Therefore, we only need to show that the value of $\Gamma_{ep}^0(78^\circ\text{K})$ which is obtained from the data at 78°K by using $b_{ep}(78^\circ\text{K})=(5.94)$ reproduces successfully the value of $\Gamma_{ep}^0(295^\circ\text{K})$ which is obtained independently from the optical data at 295°K using $\tilde{b}_{ep}(295^\circ\text{K}) = 1.22$. From the optical data, we have

$$\Gamma_{ep}^0(78^\circ\text{K}) = 1.41 \times 10^{13} \text{ sec}^{-1}$$

$$\Gamma_{ep}^0(295^\circ\text{K}) = 1.12 \times 10^{14} \text{ sec}^{-1} \quad \text{VII-(15)}$$

each of which has been obtained independently with $\textcircled{H} = 375^\circ\text{K}$.

On the other hand, Table V gives us

$$J_5^0(295^\circ\text{K}) = 0.5$$

$$J_5^0(78^\circ\text{K}) = 50$$

so that

$$\begin{aligned} \Gamma_{ep}^0(295^\circ\text{K}) &= \Gamma_{ep}^0(78^\circ\text{K}) \times \left(\frac{295}{78}\right)^5 \left(\frac{J_5^0(295^\circ\text{K})}{J_5^0(78^\circ\text{K})}\right) \\ &= 1.17 \times 10^{14} \text{ sec}^{-1} \end{aligned} \quad \text{VII-(16)}$$

Comparing this with the value, 1.12×10^{14} sec.⁻¹ of (15), we find that the two values agree within 5%. Since use of $\tilde{b}_{ep}(\alpha)$ was essential in obtaining the values of (15) from the optical data, the good agreement between (15) and (16) automatically establishes the validity of the temperature-dependence of b_{ep} .

Now that we have verified experimentally the temperature-dependence of the dispersion formulae, we are ready to predict various dispersion properties at any arbitrary temperature. As an illustration, we shall calculate the near infrared absorptivity and the optical constants (n,k) of aluminum at very low temperatures ($\lesssim 10^\circ\text{K}$), 375°K , 470°K , and 570°K in addition to the values at 78°K and 295°K which are already available from the optical data of Golovashkin et al (1960).

In the spectral range defined by

$$0.8 \mu \lesssim \lambda \lesssim 3.5 \mu$$

we use the formula,

$$\begin{aligned} A_B &\cong \frac{2}{\omega_0} \tilde{\kappa}_0 \tilde{G}_0 \\ &\cong \frac{2}{\omega_0} \left[R_{ep} \frac{1}{\alpha^5} J_5^0(\alpha) \tilde{b}_{ep}(\alpha) + R_{ee} \frac{1}{\alpha^2} + \frac{\omega^2}{\kappa_{ee}} \right] \end{aligned} \quad \text{VII-(17)}$$

In the same spectral range, the formula for the index of refraction is

$$\begin{aligned} n &\cong \frac{1}{2} \frac{\omega_0}{\omega^2} \left[\tilde{\kappa}_0 + \frac{\omega^2}{\kappa_{ee}} \right] \\ &= \frac{1}{4} \left(\frac{\omega_0}{\omega} \right)^2 A_B \end{aligned} \quad \text{VII-(18)}$$

where (17) is to be used for A_B , and k is nearly independent of temperature and is $\approx \left(\frac{\omega_0}{\omega}\right)$.

Upon using the numerical values of various parameters given in Table IX and V, we obtain

$$R_{ee} = 7.0 \times 10^{12} \text{ sec}^{-1}$$

$$R_{ep} = 7.7 \times 10^{14} \text{ sec}^{-1}$$

$$\Omega_{ee} = 1.34 \times 10^{16} \text{ sec}^{-1}$$

and thus (17) becomes

$$A_B \cong \left\{ (0.0103) \frac{10}{\alpha^5} J_s^0(\alpha) \tilde{b}_{ep}(\alpha) + \frac{3.51 \times 10^{-2}}{\lambda^2} \right\} \quad \text{VII-(19)}$$

The values of $A=(A_B+A_S)$ are plotted at the temperatures, $T \lesssim 10^\circ\text{K}$, 78°K , 295°K , 375°K , 470°K , and 570°K in Figures 25 ~ 26. The values of n are plotted in Figure 27. The absorptivity describes a straight line when plotted against $\left(\frac{1}{\lambda^2}\right)$, while n describes a straight line as a function of λ^2 . In obtaining the values of A , we have used $A_S=0.004$ as the skin absorptivity.

It should be noted that if the Umklapp processes were completely absent, the second term of (19) would vanish and A_B would be independent of λ . The curves of Figure 25 are then replaced by a family of horizontal lines, while the straight lines of Figure 27 for n should all pass through the origin.

Finally, it may be said that calculations similar to what

has been done on aluminum can be made on any other metal for which optical data are available. This applies to all the metals that have been investigated in the present chapter except for solid bismuth. The optical data^{on}/bismuth show extremely anomalous behavior, as shown by the curves of σ and $(1-\epsilon)$ in Figure 32. Whether the anomaly is due to oxides or due to some peculiar properties of the lattice is yet to be determined. While both the present and all the existing theories completely fail to explain the peculiar dispersion properties of solid bismuth that are observed by Markov and Khaikin (1960), Table III shows that the liquid bismuth is explained even by the classical Drude theory (Kent, 1919), and hence by the present theory also.

VII-(D) Determination of Impurity Contributions

Unlike the d.c. electrical properties, the optical dispersion properties are affected very little by the presence of a small amount of impurities (i.e., $\sim 10^{-4}$ or less in concentration) except at the far infrared and low temperatures. It is well known that the impurity contributions give rise to the finite residual resistance important at very low temperatures. The pronounced effect of the impurity scattering at very low temperature is attributed to the fact that the damping coefficients $\Gamma_{ep}^0(\alpha)$ and Γ_{ee}^0 vanish with $\sim T^5$ (or $\sim T^3$ for transition metals) and $\sim T^2$, respectively, when T is decreased to the neighborhood of the absolute zero, while Γ_M^0 being independent of temperature, maintains its constant value even at $0^\circ K$.

In the present theory, however, the damping coefficients Γ_{ep}^0 and Γ_{ee}^0 appear multiplied by the respective quantum correction factors $b_{ep}(\omega, T)$ and $b_{ee}(\omega)$ which, at very low temperatures and in the near infrared, increase exactly as fast as the rate at which Γ_{ep}^0 and Γ_{ee}^0 decrease with decrease in T . As a result, the over-all damping coefficient $\Gamma(\omega, T)$ manages to maintain a constant but relatively large value even at $0^\circ K$. For this reason, it will be senseless to attempt to determine the value of Γ_M^0 from a near infrared optical data unless the concentration of impurities is sufficiently large as to make Γ_M^0 comparable with R_{ee} or R_{ep} . It was shown

in chapter V that, unlike ϵ , $(1-\epsilon)$ depends on the ω -independent damping $\bar{\Gamma}_0$ such that

$$1 - \epsilon \approx \frac{\omega_0^2}{\omega^2 + (\bar{\Gamma}_M^0)^2} \quad \text{VII-(20)}$$

at very low temperatures. Unless the wavelength is very long, however, this is not going to improve the situation since in most of the infrared and near infrared regions of spectrum, (20) is replaced by $\approx \left(\frac{\omega_0}{\omega}\right)^2$.

Therefore, it is quite clear that any attempt to determine $\bar{\Gamma}_M^0$ can be made only when the optical data are available in the far infrared region, $\hbar \ll \beta \hbar \omega \lesssim \alpha$. In this case, the formula (20) is useful provided that ω is not much larger than $\bar{\Gamma}_M^0$.

At very low temperatures ($T \lesssim 10^\circ\text{K}$) and in the far infrared, the optical quantity which is measured with relative ease is the absorptivity A or the reflectivity $R=(1-A)$. The value of $\bar{\Gamma}_M^0$ can then be determined from the formulae that are given in Chapter VIII. For many metals, the values of $\bar{\Gamma}_{ee}^0$, $\bar{\Gamma}_{ep}^0$ and ω_0 are available from the room temperature data with an accuracy of 10% or less, so that if A_B is measured up to $\lesssim 10\%$, the value of $\bar{\Gamma}_M^0$ can be determined up to $\lesssim 10\%$. The optical estimation of $\bar{\Gamma}_M^0$ can be useful when a direct electrical measurement is difficult.

When the value of $\bar{\Gamma}_M^0$ is available, the impurity

concentration N_M can be estimated from the complete expression for Γ_M^o (Gurzhi, 1959) or qualitatively from

$$N_M \sim (\nu_F \tau_M)^{-3} = \left(\frac{\Gamma_M^o}{\nu_F} \right)^3 \quad \text{VII-(21)}$$

which gives us the order-of-magnitude estimation, where $(\nu_F \tau_M)$ is the mean free path of the electron-impurity collisions.

Chapter VIII

Bulk Absorption at Very Low Temperatures

VIII-(A) Normal Metals at Very Low Temperatures:

It was shown in the preceding chapters that the bulk absorptivity A_B of a normal metal (i.e., non-superconducting) retains a finite non-zero value even at 0°K in the spectral range given by $\mu \gg \alpha \gg 1$, and vanishes at 0°K , for a pure metal in the limit $\omega \rightarrow 0$. It was also shown that the bulk absorptivity at 0°K , which we shall call the "zero-point bulk absorptivity", in the near infrared is independent of ω aside from the Umklapp term.

Specifically, we obtained the following formulae for the bulk absorptivity in the high frequency part of the infrared;

$$A_B \approx \frac{2}{\omega_0} \mathcal{N}_0 G_\sigma \left[1 - \frac{9}{8} \left(\frac{\mathcal{N}_0}{\omega} \right)^2 + \frac{37}{32} \left(\frac{\mathcal{N}_0}{\omega} \right)^4 + \dots \right]$$

$$: \omega > \mathcal{N}_0 \quad (\mu > \alpha)$$

VIII-(1)

and

$$A_B \approx \frac{2}{\omega_0} \tilde{\mathcal{N}}_0 \tilde{G}_\sigma : \omega \gg \tilde{\mathcal{N}}_0 \quad (\mu \gg \alpha)$$

VIII-(2)

where

$$\begin{pmatrix} \mathcal{N}_0 \\ \tilde{\mathcal{N}}_0 \end{pmatrix} = \Gamma_{ep}^0 \begin{pmatrix} b_{ep}(\mu, \alpha) \\ \tilde{b}_{ep}(\alpha) \end{pmatrix} + \Gamma_{ee}^0 + \Gamma_M^0$$

$$G_\sigma = \left(1 + \frac{\omega^2}{\mathcal{N}_0 \mathcal{N}_{ee}} \right)$$

$$\tilde{G}_\sigma = \left(1 + \frac{\omega^2}{\tilde{\mathcal{N}}_0 \mathcal{N}_{ee}} \right)$$

VIII-(3)

and $(G_{\sigma} - 1)$ and $(\tilde{G}_{\sigma} - 1)$ can differ from zero only when the Umklapp processes are present.

It is the purpose of the present work to compute the absorptivity A_B at very low temperatures in the spectral ranges defined by

$$(i) \quad \alpha \gg \mu \gg 1$$

$$(ii) \quad \alpha \gg \mu, \mu \sim 1$$

VIII-(4)

both of which are in the far infrared. At $T \approx 0^\circ \text{K}$, the condition (i) applies for practically all frequency values of infrared, and the calculated value of A_B would then represent the far infrared zero-point bulk absorptivity.

It was explained in Chapter V that the generalized Hagen-Rubens formula

$$A_B = 2 \sqrt{\frac{\nu}{\sigma_0}} \left[1 + \frac{\Gamma_{ep}^0}{\Gamma_0^0} (b_{ep} - 1) \right]^{\frac{1}{2}}$$

VIII-(5)

applies in the far infrared when the temperature is not too low. We recall that the formula (5) was obtained by taking $\omega^2 \ll \Omega_0^2, \bar{\Omega}_0^2$.

At very low temperatures, however, ω^2 may not be

necessarily smaller than \mathcal{N}_o^2 and $\bar{\mathcal{N}}_o^2$ in the far infrared, since $\bar{\mathcal{N}}_o$, being independent of ω , decreases rapidly to Γ_M^o with decrease in T and \mathcal{N}_o^2 likewise may have a small value if the quantum correction factor $b_{ep}(\mu, \alpha)$ does not counteract sufficiently the rapid decrease of $\Gamma_{ep}^o(\alpha)$ with decrease in T .

Therefore, it is quite clearly the primary task of the present work to investigate the ω -dependence of $b_{ep}(\mu, \alpha)$ in the spectral ranges of (4) and also to specify the order of magnitude of Γ_M^o relative to the values of ω in these spectral ranges. We shall first investigate the ω -dependence of $b_{ep}(\mu, \alpha)$ for $\mu \gg 1$ and $T \cong 0^\circ K$. We shall, for the sake of generality, calculate it for both $\mu > \alpha$ and $\mu < \alpha$.

Upon using various formulae for $J_n(\mu, \alpha)$ and $K_n(\mu, \alpha)$ in the results of Chapters IV, V, and VI, we obtain the following expressions for $b_{ep}(\mu, \alpha)$ for both transition and nontransition metals;

$\mu > \alpha$:

$$b_{ep}(\mu, \alpha) \approx \frac{\alpha^5}{10} \left[1 - \frac{5}{6} \frac{\alpha}{\mu} \right] / J_3^o(\alpha)$$

VIII-(6)

$$\mu < \alpha :$$

$$b_{ep}(\mu, \alpha) \approx \frac{\mu^5}{60} / J_5^0(\alpha)$$

VIII-(7)

for nontransition metals, and

$$\mu > \alpha :$$

$$b_{ep}(\mu, \alpha) \approx \frac{\alpha^3}{6} \left[1 - \frac{3}{4} \frac{\alpha}{\mu} \right] / J_3^0(\alpha)$$

VIII-(8)

$$\mu < \alpha :$$

$$b_{ep}(\mu, \alpha) \approx \frac{\mu^3}{24} / J_3^0(\alpha)$$

VIII-(9)

for transition metals, where, for the sake of convenience, we have taken α_E to be zero.

Thus, the electron-phonon damping coefficient of non-transition metals is given by

$$\Gamma_{ep}(\mu, \alpha) \approx \frac{R_{ep}}{10} \left(1 - \frac{5}{6} \frac{K\Theta}{\hbar\omega} \right) : \mu > \alpha$$

VIII-(10)

$$\approx \frac{R_{ep}}{60} \left(\frac{\hbar\omega}{K\Theta} \right)^5 : \mu < \alpha$$

VIII-(11)

For transition metals with $\alpha_E \cong 0$, we have

$$\Gamma_{ep}^{sd}(\mu, \alpha) \approx \frac{R^{sd}}{6} \left(1 - \frac{3}{4} \frac{K_H}{\hbar\omega} \right) : \mu > \alpha \quad \text{VIII-(12)}$$

$$\approx \frac{R^{sd}}{24} \left(\frac{\hbar\omega}{K_H} \right)^3 : \mu < \alpha \quad \text{VIII-(13)}$$

It must be remembered that, for a ferromagnetic metal, the equations (12) and (13) must be multiplied by 1/2 on the R.H.S. as the correction for the residual magnetization. The formulae (8), (9), (12) and (13) will also apply to those transition metals which have $\alpha_E > 0$ provided that α_E is sufficiently smaller than α . In this case, the formulae (9) and (13) are multiplied by $(1 - \frac{\alpha_E}{\mu})$ so that $\Gamma_{ep}^{sd}(\mu, \alpha)$ has non-zero values for $\hbar\omega > K_H$ only.

For both types of metals, the electron-electron damping coefficient is given by

$$\Gamma_{ee}(\mu, \alpha) \approx \frac{1}{4\pi^2} R_{ee} \left(\frac{\hbar\omega}{K_H} \right)^2 \quad \text{VIII-(14)}$$

In order to write down the formulae for the bulk absorptivity, we need to compare the magnitudes of ω^2 with \mathcal{N}_o^2 , $\bar{\mathcal{N}}_o^2$: i.e., to find out which of the equations (1) and (5) is applicable.

At $T \cong 10^{\circ} \text{K}$, $\mu = 1$ corresponds to the values of ω which is of the order of $\sim 10^{12} \text{ sec}^{-1}$. We are therefore interested in the spectral range given by

$$10^{12} \lesssim \omega \ll \frac{K(\Theta)}{h} \cong 10^{13} \sim 10^{14} \text{ sec}^{-1}$$

It was shown in preceding chapters that R_{ep} (and R_{ep}^{sd}), R_{ee} and Γ_M° (for a "pure" metal) have typical values of the order of $10^{13} \sim 10^{14}$, $10^8 \sim 10^{10}$, and $\lesssim 10^{10}$, respectively. The Debye temperature is generally of the order of several hundred $^{\circ} \text{K}$ corresponding to a ω of $10^{13} \sim 10^{14} \text{ sec}^{-1}$.

Therefore, for $\omega \cong 10^{12} \text{ sec}^{-1}$ and $\Theta \cong 100^{\circ} \text{K}$, we have

$$\omega^2 \gg \mathcal{N}_o^2$$

The same is then true for $\bar{\mathcal{N}}_o^2$ since it contains no ω -dependence and

$$\bar{\mathcal{N}}_o \approx (\Gamma_M^{\circ} + \Gamma_{ee}^{\circ}) \ll \omega \cong 10^{12} \text{ sec}^{-1}$$

This implies that the equation (1) is to be used for evaluating

the absorptivity in the spectral range of $\omega \gtrsim 10^{12} \text{ sec}^{-1}$
and $T < 10^0 \text{ K}$.

Thus we have the following formulae for the bulk
absorptivity of the noble metals and the transition metals,
respectively;

$$\mu > \alpha:$$

$$A_B \approx \frac{2}{\omega_0} \left\{ \frac{R_{ep}}{10} \left(1 - \frac{5}{6} \frac{K_{\oplus}}{\hbar\omega} \right) + \frac{1}{4\pi^2} R_{ee} \left(\frac{\hbar\omega}{K_{\oplus}} \right)^2 + \Gamma_M^0 \right\}$$

VIII-(15)

$$\mu < \alpha:$$

$$A_B \approx \frac{2}{\omega_0} \left\{ \frac{R_{ep}}{60} \left(\frac{\hbar\omega}{K_{\oplus}} \right)^5 + \frac{1}{4\pi^2} \left(\frac{\hbar\omega}{K_{\oplus}} \right)^2 + \Gamma_M^0 \right\}$$

VIII-(16)

for nontransition metals, and

$$\mu > \alpha:$$

$$A_B^{sd} \approx \frac{2}{\omega_0} \left\{ \frac{\chi(0)}{2} \frac{R^{sd}}{6} \left(1 - \frac{3}{4} \frac{K_{\oplus}}{\hbar\omega} \right) + \frac{1}{4\pi^2} R_{ee} \left(\frac{\hbar\omega}{K_{\oplus}} \right)^2 + \Gamma_M^0 \right\}$$

VIII-(17)

$$\mu < \alpha:$$

$$A_B^{sd} \approx \frac{2}{\omega_0} \left\{ \frac{\chi(0)}{2} \frac{R^{sd}}{24} \left(\frac{\hbar\omega}{K_{\oplus}} \right)^3 + \frac{1}{4\pi^2} R_{ee} \left(\frac{\hbar\omega}{K_{\oplus}} \right)^2 + \Gamma_M^0 \right\}$$

VIII-(18)

for transition metals, where $X(0) = 1$ for ferromagnetic metals and $= 2$ for paramagnetic metals.

Although R_{ee} is generally smaller than R_{ep} by a large factor, contributions of the electron-electron collisions to (15)~(18) can be substantially large compared with the electron-phonon term because of the smaller power of $\left(\frac{\hbar\omega}{K\Theta}\right)$ in the electron-electron term. This is even more true if, in (17) and (18), α_E is very large. The first terms inside $\{ \}$ of (17) and (18) must be equated to zero for $\hbar\omega \leq K\Theta_E$ when Θ_E is not zero so that the only ω -dependence appears in the Umklapp term.

Now let us investigate the case of $\mu \lesssim 1$ and

$$\omega \simeq \left(\frac{KT}{\hbar} \right) \lesssim 10^{12} \text{ sec}^{-1}$$

This spectral range is of interest when one wishes to compare the absorption of a normal metal since the superconducting energy gap is generally of the order of several ^0K in temperature and thus $\omega \lesssim 10^{12} \text{ sec}^{-1}$. For $\omega \sim 10^{11} \text{ sec}^{-1}$, we will in general have $\left(\frac{\hbar\omega}{K\Theta}\right) \lesssim 10^{-2}$ for $\Theta \gtrsim 100^\circ\text{K}$. This implies that we will have Γ_M^0 as the most dominant term in both \mathcal{N}_0 and $\bar{\mathcal{N}}_0$ when the metal is not completely free of impurities. However, since we saw previously that $\Gamma_M^0 \lesssim 10^{10} \text{ sec}^{-1}$ for most of the so called "pure" metal samples, we still have

$$\left(\frac{\mathcal{N}_0}{\omega}\right), \left(\frac{\bar{\mathcal{N}}_0}{\omega}\right) \lesssim \frac{1}{10}$$

so that the equation (1) is again applicable.

Therefore, we shall henceforth consider (1) as the general formula for bulk absorptivity which is applicable in the far infrared at very low temperatures regardless of whether $\mu \gg 1$ or $\mu \simeq 1$, unless a metal has an exceptionally large value of Γ_M^0 . When the sample has a large Γ_M^0 , $\gtrsim 10^{12} \text{ sec}^{-1}$, say, the Hagen-Rubens formula (5) should be used with $\Gamma^0(\alpha)$ equated to Γ_M^0 .

For $\alpha \gg \mu$ and $\mu \lesssim 1$, we have the following formulae for $J_n(\mu, \alpha)$ and $K_n(\mu, \alpha)$;

$$J_n(\mu, \alpha) \approx \frac{2}{e^{2\mu} - 1} \left[\mu J_n^0(\alpha) + \mu^3 \frac{n(n-1)}{3!} J_{n-2}^0(\alpha) + \dots \right]$$

$$K_n(\mu, \alpha) \approx \frac{2}{e^{2\mu} - 1} \left[\mu K_n^0(\alpha) + \mu^3 \frac{n(n-1)}{3!} K_{n-2}^0(\alpha) + \dots \right] \quad \text{VIII-(19)}$$

where the first terms inside $\left[\dots \right]$ are the largest terms. These formulae are to be used in evaluating $b_{ep}(\mu, \alpha)$,

$$b_{ep}(\mu, \alpha) = \frac{e^\mu \sinh \mu}{\mu} \left[J_5(\mu, \alpha) - \mu \frac{(e^\mu - 1)^2}{(e^{2\mu} - 1)} [J_4 + 2K_4] \right] \quad \text{VIII-(20)}$$

for nontransition metals, and

$$b_{ep}(\mu, \alpha) = \frac{e^{\mu} \sinh \mu}{\mu} \left[\bar{J}_3(\mu, \alpha) - \mu \frac{(e^{\mu} - 1)^2}{e^{2\mu} - 1} \left[\bar{J}_2(\mu, \alpha) + 2 \bar{K}_2(\mu, \alpha) \right] \right]$$

VIII-(21)

for transition metals. Then, it is a trivial matter to write down the bulk absorptivity since we only need to replace b_{ep} of (16)~(18) by (20) and (21) in the electron-phonon term.

Finally, it may be reminded that the values of the parameters R_{ep} , R_{ee} , and R_{ep}^{Sd} which are required for a numerical estimation of (16)~(18) are to be obtained from the optical data taken at higher temperatures and alternatively from the d.c. electrical data. The same applies to the other parameters.

VIII-(B) Bulk Absorption by Superconductors:

Compared with what are available on normal metals, very little experimental data are available on the optical and infra-red absorption in superconductors. Some of the latest measurements are those of Biondi and Garfunkel (1959) and Richards and Tinkham (1960). These measurements are designed to determine the superconducting energy gap from the shape of the observed absorption curves. Specifically, these experiments include measuring the absorption of the external electromagnetic wave in a superconductor relative to that in a normal metal, and the results are embodied in the curves showing the ratio,

$$r_{SN} = 1 - \frac{A_S}{A_N} \quad \text{VIII-(22)}$$

where A_S and A_N are the absorptivities, at a given frequency and temperature, of the superconducting and normal metal, respectively. The normal state of metal is accomplished by applying a magnetic field parallel to the surface which is strong enough to reduce the gap to zero. The results are equivalently expressed in terms of the power absorbed, P_S and P_N , instead of the absorptivities A_S and A_N . In the plot of r_{SN} vs. ω , for instance, the energy gap is determined by locating the frequency ω_g where r_{SN} starts to decrease abruptly: that is, the head of the absorption tail.

The superconductor differs from the normal state in that the density-of-states function $\rho(E)$ does not show the continuous distribution around the Fermi level in the form,

$$\rho(E) = \text{constant} \times \sqrt{E}$$

but possesses discontinuities exhibiting a forbidden region on both sides of the Fermi level.

In the theory of Bardeen, Cooper, and Schrieffer (1957), a certain minimum energy is required to produce an excitation from the ground state. This minimum excitation energy, or the energy gap, is a central result of the BCS theory. Existence of the predicted energy gap has been fully verified, and is by now a popularly accepted fact. According to the theory of BCS, the density-of-states function $\rho_S(E)$ of a superconductor is given by

$$\begin{aligned} \rho_S(E) &= \rho_N(0) \left| \frac{z}{[z^2 - \epsilon^2]^{\frac{1}{2}}} \right| & : |z| > \epsilon \\ &= 0 & : |z| < \epsilon \end{aligned}$$

VIII-(23)

where $\rho_N(0)$ is the density-of-states function of a normal metal evaluated at the Fermi level, ϵ is (1/2) of the energy

gap E_g which is a function of temperature, and

$$z = (E - E_F)$$

It is seen that $\rho_s(E)$ increases very sharply at the gap edges, $E = (E_F \pm \epsilon)$. The energy gap $E_g(T)$ achieves its maximum value $E_g(0)$ at $T = 0^\circ\text{K}$ and decreases to zero as T is increased to T_c , the superconducting transition temperature. In the region where $E < E_F - \epsilon$, all the electrons occur paired and this part of the band is called the paired band. On the other hand, the electrons in the region where $E > E_F + \epsilon$ are unpaired, and this part of the band is usually referred to as the unpaired band or the "normal" conduction band which bears no difference from the conduction band of a normal metal. However, at a temperature T below T_c , most of the electrons are paired, and very few are available in the unpaired band. Therefore, most of the absorption will be due to these paired electrons. When the paired electrons make transitions to the unpaired band, the energy absorbed must be at least as much as that which is required to overcome the gap E_g : otherwise, no transition of this type is possible, since electrons are forbidden in the gap. The BCS density-of-states function $\rho_s(E)$ is schematically illustrated in Figure 35. The typical temperature dependence of E_g is shown in Figure 36. For $T > T_c$,

the metal is completely normal, and absorptivity is fully described by the results obtained in VIII- (A). The curve showing the dependence of E_g on the magnetic field H bears a close resemblance to that of Figure 36 when we replace T by H and T_c by a certain critical field strength H_c . Thus, when $H > H_c$, the metal is completely normal even if $T < T_c$, and the optical properties are satisfactorily described by the results obtained in VIII- (A) and also in the preceding chapters.

The latest theory of optical dispersion in superconductors is due to Mattis and Bardeen (1958), who calculate the frequency dependence of the complex conductivity σ_s of superconductor on the basis of the BCS theory. Specifically, they calculate the ratios,

$$\left(\sigma(\omega, \underline{p}) / \sigma_N \right), \quad \left(\sigma_2(\omega, \underline{p}) / \sigma_N \right)$$

σ_N being the high frequency conductivity of normal metal and \underline{p} the photon propagation momentum that is involved, and where σ_1 and σ_2 are defined as

$$\sigma_s = \sigma_1 + i \sigma_2 \quad \text{VIII-(24)}$$

Based on these results, Richards and Tinkham calculate the quantity

$$r_{SN} = 1 - \frac{A_S}{A_N} = 1 - \frac{R_S}{R_N} \quad \text{VIII-(25)}$$

from the relations,

$$\frac{Z_S}{Z_N} = \left(\sigma_N / \sigma_1 + i \sigma_2 \right)^{\frac{1}{3}} \quad \text{VIII-(26)}$$

$$\begin{aligned} Z_N &= (1 + i\sqrt{3}) R_N \\ R_N &= \mathcal{R}_e(Z_N) \\ R_S &= \mathcal{R}_e(Z_S) \end{aligned} \quad \text{VIII-(27)}$$

where Z_S and Z_N are the surface impedance of superconducting and normal metals, and R_S and R_N are the respective surface resistance values.

These relations are applicable only in the extreme anomalous limit where all the contributions to the absorption and resistance come from the surface effects in which the electrons absorb photons and collide with the surface of the metal to conserve energy and momentum. Thus, they do not include the possible contributions of the bulk where electrons might absorb photons and emit phonons to conserve energy and momentum.

The bulk contribution of this kind has been found to be significant in normal metals and was fully discussed theoretically in VIII- (A) and preceding chapters. That the bulk effects might also be significant in a superconductor on account of the large electron-phonon interactions that are present was suggested by Richards and Tinkham (1960) following the similar suggestion by Holstein (1952) for a normal metal.

Richards and Tinkham compared the experimental absorption-edge curves for superconducting lead and tin with the curve predicted by the theory of Mattis and Bardeen. The comparison shows that although they agree qualitatively as far as the shape of the absorption-edge is concerned, the theoretical values are much greater than the measured values. Further, the theoretical curve tails off much slower than the observed edge. This is shown in Figure 38 where ϵ_{SN} is plotted against the ratio (ω/ω_g) for ω greater than $\omega_g = (E_g/\hbar)$. At the present, no positive explanations are available on the discrepancy between the theoretical and experimental absorption edges shown in Figure 38. Since the theoretical curve of Mattis and Bardeen is obtained by considering the anomalous skin effects only, it might perhaps be worthwhile to follow the suggestion of Richards and Tinkham and compute the bulk contributions to the absorptivity. If the bulk contribution is significant at all, it could very well effect in reducing the theoretical values of

Mattis and Bardeen, although it is not certain as to whether the magnitude of the bulk absorption is of the right order as to bridge the gap between the theory and experiment.

For $\omega < \omega_g$, Schrieffer (1959) derived the formula

$$\epsilon_{SN} \approx \frac{1}{\hbar\omega} \int_{\epsilon}^{\infty} \frac{(E_1 E_2 + \epsilon^2) [F(E_1) - F(E_2)]}{[(E_1^2 - \epsilon^2)(E_2^2 - \epsilon^2)]^{\frac{1}{2}}} dE_1$$

VIII-28

from the BCS theory assuming a symmetric electron-phonon interaction coefficients. This formula applies in the spectral range of $\frac{1}{2} \omega_g < \omega < \omega_g$

and differs from zero only for $T > 0^\circ K$.

Richards and Tinkham (1960) checked this formula in the above spectral range and found good agreement with the experimental absorption data. The formula (28) is plotted in Figure 37. It is shown that ϵ_{SN} rises slowly with increase in ω and is smaller than unity only by a small fraction. Experimental curves of ϵ_{SN} show that the rise of ϵ_{SN} with increase in ω is pronounced in some superconductors such as the transition metals vanadium and indium while others have a nearly flat ϵ_{SN} for $\omega < \omega_g$. At any rate, it is certain that the ϵ_{SN} curves do have their peaks, which are very likely to be discontinuous because of the discontinuity of ρ_S at the gap edges, at $\omega = \omega_g$ and tails off rapidly as ω is increased further beyond ω_g .

In what follows, we shall do our calculations for the bulk absorptivity only for $\omega > \omega_g$ and at $T = 0^\circ\text{K}$. The theoretical method is essentially the same as in the preceding chapters, and the difference will be in that we now have to use the new density-of-states function $\rho_S(E)$ that is offered by the BCS theory.

The density-of-states function ρ_S and the Fermi function $F(E)$ define the number of electrons per unit volume by the relation,

$$\begin{aligned} n^0 &= n_- + n_+ \\ &= 2 \left[\int_{-\infty}^{-E} dz + \int_{+E}^{+\infty} dz \rho_S(z) F(z) \right] \\ &\quad : z = (E - E_F) \end{aligned} \quad \text{VIII-(29)}$$

where n_- is the number of paired electrons per unit volume and n_+ is the number of unpaired electrons per unit volume. At 0°K , we have $n_+ = 0$ and the second integral vanishes.

Probability per unit time and per unit energy range that an electron initially at the state E_1 makes a transition to the final states in the range $E_2 \rightarrow (E_2 + dE_2)$ is given by

$$\frac{\Delta P}{\Delta E_2} \propto P(E_1 \rightarrow E_2) \rho_S(E_2) [1 - F(E_2)]$$

and hence

$$P(E_1) \propto \int dE_2 \rho_S(E_2) [1 - F(E_2)] P(E_1 \rightarrow E_2) \quad \text{VIII-(30)}$$

Similarly, the average of $P(E_1)$ over all the initial states is given by

$$\langle P \rangle \propto \iint dE_1 dE_2 \rho_S(E_1) \rho_S(E_2) F(E_1) [1 - F(E_2)] P(E_1 \rightarrow E_2) \quad \text{VIII-(31)}$$

where it is implicit that the surface integrals have already taken care of the necessary requirements of conservation of energy and momentum.

Upon comparing (30) and (31) with the corresponding equations for a normal metal in Chapter IV, it is readily shown that the expression for the power expenditure $\bar{W}_S^{(r)}$ of a superconductor will involve the function $F_{(s)}^{(r)}$ in the form,

$$F_{(s)}^{(r)}(q) = \frac{1}{\beta} \frac{1}{\rho_{N(0)}^2} \int_{-\infty}^{+\infty} dx \frac{1}{1 + e^{x+a}} \frac{e^x}{1 + e^x} \rho_S(x) \rho_S(x+a) \quad \text{VIII-(32)}$$

where

$$a = \beta(r E_q + s \hbar \omega)$$

We have only $F_{(-)}^{(+)}$ to consider and other three vanish at

$T=0^\circ \text{K}$. Further, the integrand

$$\frac{e^x}{1+e^x} \frac{1}{1+e^{x+a}}$$

is different from zero only for those values of a which satisfies the inequality,

$$0 < x < -a \quad \text{VIII-(33)}$$

The possible values of x are further restricted due to the presence of the energy gap: namely, the condition expressed by (23),

$$|x+a|, |x| > \beta\epsilon \quad \text{VIII-(34)}$$

for the product, $\rho_s(x) \rho_s(x+a)$, not to vanish.

Combination of (33) and (34) immediately yields the inequality condition,

$$\beta\epsilon < x < -(a+\epsilon)\beta$$

$$2\epsilon < -a \quad \text{VIII-(35)}$$

The integral (32) thus reduces to the form,

$$F_{(t)}^{(+)}(q) \approx \int_{\epsilon}^{-(a+\epsilon)} dy \frac{|y||y+a|}{[(y^2-\epsilon^2)((y+a)^2-\epsilon^2)]^{\frac{1}{2}}}$$

VIII-(36)

For $\hbar\omega < K\Theta$, we obtain the following expression for the power expenditure per unit volume per unit time;

$$\bar{W}_S \cong \frac{3\pi}{4} \frac{e^2 g^2 N_p E^2}{n_0 M (K\Theta)^6 \omega^2} \times$$

$$\int_0^{\hbar\omega - E_g} \zeta^4 d\zeta \int_{\epsilon}^{\hbar\omega - \zeta - \epsilon} dx \frac{|x| |x + \zeta - \hbar\omega|}{\{[x^2 - \epsilon^2][(x + \zeta - \hbar\omega)^2 - \epsilon^2]\}^{\frac{1}{2}}}$$

VIII-(37)

The absorptivity A_s is then readily obtained as

$$A_s \approx \sqrt{\frac{m^*}{\pi n_- e^2}} \frac{R}{60} \left(\frac{\hbar\omega}{K\Theta} \right)^5 (1 - r_{SN})$$

VIII-(38)

where

$$(1 - r_{SN}) \cong \frac{6}{(\hbar\omega)^5} \int_0^{(\hbar\omega - E_g)} \zeta^4 d\zeta \int_{\epsilon}^{(\hbar\omega - \zeta - \epsilon)} dx \frac{|x| |x + \zeta - \hbar\omega|}{\left\{ [x^2 - \epsilon^2] [(x + \zeta - \hbar\omega)^2 - \epsilon^2] \right\}^{\frac{1}{2}}}$$

VIII-(39)

where R is exactly the same as R_{ep} if we take

$$n_- + n_+ \cong n_- \cong n_0$$

VIII-(40)

: i.e., all conduction electrons are in the paired band at
 $T \cong 0^\circ K$

The formula (39) is good only when the Umklapp processes and impurity scattering can be ignored in the normal metal. Otherwise, we must use the more general formula,

$$1 - r_{SN} \cong \frac{1}{1 + \frac{15}{\pi^2} \frac{R_{ee}}{R} \left(\frac{K\Phi}{\hbar\omega}\right)^3 + 60 \frac{\Gamma_M^0}{R} \left(\frac{K\Phi}{\hbar\omega}\right)^5} \times$$

$$\frac{6}{(\hbar\omega)^5} \int_0^{(\hbar\omega - E_g)} \zeta^4 d\zeta \int_{\epsilon}^{(\hbar\omega - \zeta - \epsilon)} dx \frac{|x| |x + \zeta - \hbar\omega|}{\left\{ [x^2 - \epsilon^2] [(x + \zeta - \hbar\omega)^2 - \epsilon^2] \right\}^{\frac{1}{2}}}$$

VIII-(41)

The integrals of (33) and (35) are difficult to evaluate exactly because of the discontinuity in the density-of-states functions.

However, a simple, and perhaps oversimplified, approximation can be obtained upon noting that the first factor in the integrand represents the density of states of the initial states and the second factor represents that of the final states, and that, at $T = 0^\circ \text{K}$, most transitions involve only those initial states which lie at the lower edge of the gap: i.e.,

$$E_i \cong E_F - \epsilon, \quad \epsilon \approx \epsilon$$

This means that most of the contribution to integral (37) comes from the lower limit of the integral, although the apparent form of the formula tends to show that the integrand has singularity at the upper limit as well as at the lower limit. The singularity at the upper limit has to do with the fact that most of the electrons reaching the unpaired band as the result of transitions are likely to crowd at the upper edge of the gap, where the density-of-states function is large. We thus have

$$F_{(-)}^{(+)}(\eta) \approx (\hbar\omega - E_\eta - \epsilon) : > + \epsilon$$

VIII-(42)

where it is implicit that the integral in q is to include only those values which make $F_{(-)}^{(+)} > +\epsilon$. After some necessary mathematical steps, we find that r_{SN} of (39) reduces to the simple formula,

$$1 - r_{SN} \approx \left(1 - \frac{E_g}{\hbar\omega}\right)^5 \left(1 + 2 \frac{E_g}{\hbar\omega}\right)$$

$$: \hbar\omega < K^{\oplus}$$

VIII-(43)

The expressions for A_s and r_{SN} of a transition metal may be obtained in the same manner. In particular, for those transition metals which have $\alpha_E = 0$, the formula for r_{SN} which is equivalent to (43) is readily obtained as

$$1 - r_{SN} \approx \left(1 - \frac{E_g}{\hbar\omega}\right)^2 \left(1 - \left(\frac{E_g}{\hbar\omega}\right)^2\right)$$

VIII-(44)

The formulae (43) and (44), unfortunately, fail to improve the agreement with the experimental values of Figure 38. For a more rigorous comparison, however, we have to obtain a numerical solution to the complete integral of (39). This would certainly improve the situation since the assumption that was adopted in obtaining the crude solutions (43) and (44), was to restrict absorptive transitions to only those pairs lying at

the edge of the gap, while the complete integral takes into consideration the transitions of any electrons in the paired band, thus increasing the value of $(1 - r_{SN})$.

APPENDIX I
Calculation of $J_n(\alpha)$

$$J_n^0(\alpha) = \int_0^\alpha x^n dx / (e^x - 1)(1 - e^{-x}) : n > 0 \quad \text{I-(1)}$$

I-A: $\alpha \ll 1$

$$\begin{aligned} J_n^0(\alpha) &\approx \int_0^\alpha x^{n-2} dx \left[1 - \frac{7}{12} x^2 + \dots \right] \\ &= \frac{1}{n-1} \alpha^{n-1} - \frac{7}{12} \frac{1}{n+1} \alpha^{n+1} + \dots \end{aligned} \quad \text{I-(2)}$$

I-B: $\alpha \gg 1$

$$J_n^0(\alpha) \approx n \int_0^\infty \frac{x^{n-1} dx}{e^x - 1} = n! \sum_{m=1}^\infty \binom{-n}{m} \quad \text{I-(3)}$$

e.g.,

$$J_5^0(\alpha) = 124.4$$

I-C: General calculation

$$J_n^0(\alpha) = \int_0^\alpha \frac{e^x x^n dx}{(e^x - 1)^2} = n \int_0^\alpha \frac{x^{n-1} e^{-x} dx}{(1 - e^{-x})} - \frac{\alpha^n}{e^\alpha - 1} \quad \text{I-(4)}$$

The integral on the right-hand side can be written

$$\int_0^{\alpha} \frac{x^{n-1} e^{-x}}{1 - e^{-x}} dx = \int_0^{\infty} \frac{x^{n-1} e^{-x}}{1 - e^{-x}} dx - \int_{\alpha}^{\infty} \frac{x^{n-1} e^{-x}}{1 - e^{-x}} dx \quad \text{I-(5)}$$

The definite integral can be evaluated by the series,

$$\int_0^{\infty} \frac{x^{n-1} e^{-x}}{1 - e^{-x}} dx = (n-1)! \sum_{m=1}^{\infty} \binom{-n}{m} \quad \text{I-(6)}$$

e.g.

$$= 24.8861 \quad ; \quad n = 5$$

The indefinite integral can also be written as a series,

$$\int_{\alpha}^{\infty} \frac{x^{n-1} e^{-x}}{1 - e^{-x}} dx = \sum_{r=1}^n \frac{(n-1)!}{(n-r)!} \alpha^{n-r} \sum_{m=1}^{\infty} \binom{r}{m} e^{m\alpha} \quad \text{I-(7)}$$

Substitute Equations (5), (6) and (7) into Equation (4):

$$J_n^0(\alpha) = \left[n! \sum_{m=1}^{\infty} \binom{-n}{m} - \sum_{r=1}^n \frac{n!}{(n-r)!} \alpha^{n-r} \sum_{m=1}^{\infty} \binom{r}{m} e^{m\alpha} \right. \\ \left. - \alpha^n / (e^{\alpha} - 1) \right] \quad \text{I-(8)}$$

I-D: $J_5^0(\alpha)$

From Equation (8) we compute the numerical values of $J_5^0(\alpha)$. For small values of α :

$$\frac{1}{\alpha^4} J_5^0(\alpha) = B_0 + B_1\alpha^2 + B_2\alpha^4 + B_3\alpha^6 + B_4\alpha^8 + B_5\alpha^{10} + \dots \quad \text{I-(9)}$$

$$\begin{aligned} B_0 &= 0.25000000 \\ B_1 &= - .01388889 \\ B_2 &= 0.00052083 \\ B_3 &= - .00001653 \\ B_4 &= 0.00000096 \\ B_5 &= - .00000003 \end{aligned} \quad \text{I-(10)}$$

This series is good to 8 places for $\alpha = 1$, and its accuracy diminishes thereafter.

For somewhat larger values of α , let

$$u = \frac{1}{3} \alpha$$

Then

$$\frac{1}{\alpha^4} J_5^0(\alpha) = D_0 + D_1u^2 + D_2u^4 + D_3u^6 + \dots + D_9u^{18} \quad \text{I-(11)}$$

$$D_0 = 0.250000$$

$$D_1 = - .125000$$

$$D_2 = 0.042188$$

$$D_3 = - .012054$$

$$D_4 = 0.003164$$

$$D_5 = - .000792$$

$$D_6 = 0.000193$$

$$D_7 = - .000046$$

$$D_8 = 0.000011$$

$$D_9 = - .000003$$

I-(12)

This series is good for $\alpha < 2\pi$ and diverges for $\alpha > 2\pi$, and should not be used for values of α much larger than 3 so that the last terms contribute significantly.

APPENDIX II

Calculation of $\tilde{b}_{ep}(\alpha)$

In the limit of $\hbar\omega \gg K\theta$, the quantum correction factor $b_{ep}(\mu, \alpha)$ becomes

$$\tilde{b}_{ep}(\alpha) = \left[\frac{1}{5} + \frac{\alpha^5}{5} \left(\frac{1}{2} + \frac{1}{e^{\alpha}-1} \right) / J_5^0(\alpha) \right] \quad \text{II-(1)}$$

With the help of Appendix I, we evaluate $\tilde{b}_{ep}(\alpha)$ numerically for $\alpha < 2\pi$.

For small values of α ,

$$\tilde{b}_{ep}(\alpha) = \frac{1}{5} + \frac{A_0 + A_1\alpha^2 + A_2\alpha^4 + A_3\alpha^6 + A_4\alpha^8}{B_0 + B_1\alpha^2 + B_2\alpha^4 + B_3\alpha^6 + B_4\alpha^8 + B_5\alpha^{10}} \quad \text{II-(2)}$$

where

$$\begin{aligned} A_0 &= 0.20000000 \\ A_1 &= 0.01666667 \\ A_2 &= - .00027778 \\ A_3 &= 0.00000661 \\ A_4 &= - .00000017 \end{aligned} \quad \text{II-(3)}$$

and the B-series are the same as in Equation I-(9).

The A series are the quantity,

$$\frac{\alpha}{5} \left(\frac{1}{2} + \frac{1}{e^{\alpha}-1} \right) \cong \sum_{m=0}^{\infty} A_m \alpha^{2m} \quad \text{II-(4)}$$

$$: \alpha \lesssim 1$$

For somewhat larger values of α , let

$$u = \frac{1}{5} \alpha$$

Then

$$\tilde{b}_{ep}(\alpha) = \frac{1}{5} + \frac{C_0 + C_1 u^2 + C_2 u^4 + C_3 u^6 + \dots + C_8 u^{16}}{D_0 + D_1 u^2 + D_2 u^4 + D_3 u^6 + \dots + D_9 u^{18}} \quad \text{II-(5)}$$

$$: \alpha < 2\pi$$

$$\sum_{m=0}^{\infty} C_m u^{2m} = \frac{\alpha}{5} \left(\frac{1}{2} + \frac{1}{e^{\alpha}-1} \right) \quad \text{II-(6)}$$

$$C_0 = 0.200000$$

$$C_1 = 0.150000$$

$$C_2 = - .022500$$

$$C_3 = 0.004821$$

$$C_4 = - .001085$$

$$C_5 = 0.000247$$

$$C_6 = - .000056$$

$$C_7 = 0.000013$$

$$C_8 = - .000003$$

II-(7)

and the D-series are the same as in Equation I-(11).

Similarly, it can be evaluated for $\alpha > 2\pi$ when the formulæ of Appendix I are used.

For $\alpha \geq 17$, for instance, we obtain

$$\tilde{b}_{ep}(\alpha) = \left(\frac{1}{5} + \frac{\alpha^5}{1244.31} \right) \quad \text{II-(8)}$$

Appendix III

Integrals $J_n(\mu, \alpha)$ and $K_n(\mu, \alpha)$

III-A: General expression for $J_n(\mu, \alpha)$

$$J_n(\mu, \alpha) = \int_0^\alpha x^n dx / (e^x - e^\mu)(e^\mu - e^{-x}) : n > 0 \quad \text{III-(1)}$$

We will use the relation,

$$\frac{1}{(e^x - 1)(e^{x+2\mu} - 1)} = \frac{e^{-x}}{(e^{2\mu} - 1)} \left[\frac{1}{e^x - 1} - \frac{1}{e^{x+2\mu} - 1} \right]$$

$$\int_0^\alpha \frac{x^m dx}{e^x - 1} = \frac{x^{m+1}}{m+1} \frac{1}{e^x - 1} \Big|_0^\alpha + \frac{1}{m+1} J_{m+1}^0(\alpha)$$

where

$$\left[\frac{x^{m+1}}{e^x - 1} \right]_{x=0} = \begin{cases} 0 & : m > 0 \\ 1 & : m = 0 \end{cases}$$

Then, for $n > 0$,

$$\begin{aligned} J_n(\mu, \alpha) &= \frac{1}{e^{2\mu} - 1} \sum_{m=0}^n \frac{1}{m+1} \binom{n}{m} \mu^{n-m} \left[\frac{(\alpha-\mu)^{m+1}}{e^{\alpha-\mu} - 1} \right. \\ &\quad + (-1)^{n-m+1} \frac{(\alpha+\mu)^{m+1}}{e^{\alpha+\mu} - 1} - (-1)^{m+1} \left\{ e^\mu + (-1)^n \right\} \frac{\mu^{m+1}}{e^\mu - 1} \quad \text{III-(2)} \\ &\quad \left. + J_{m+1}^0(\alpha-\mu) + (-1)^{n-m+1} J_{m+1}^0(\alpha+\mu) - (-1)^{m+2} \left\{ 1 + (-1)^{n+1} \right\} J_{m+1}^0(\mu) \right] \end{aligned}$$

III-B: General expression for $K_n(\mu, \alpha)$

$$K_n(\mu, \alpha) = \int_0^\alpha x^n dx / \left((e^x - e^\mu) (e^\mu - e^{-x}) (e^x - 1) \right) \quad \text{III-(3)}$$

We split the three factors as follows:

$$\frac{1}{(e^x - e^\mu) (e^\mu - e^{-x})} = \frac{e^{-\mu}}{(e^{2\mu} - 1)} \left[\frac{1}{e^{x-\mu}-1} - \frac{1}{e^{x+\mu}-1} \right]$$

$$\frac{1}{(e^x - 1) (e^{x\pm\mu} - 1)} = \frac{e^{-x}}{(e^{\pm\mu} - 1)} \left[\frac{1}{e^x-1} - \frac{1}{e^{x\pm\mu}-1} \right]$$

$$\frac{1}{e^x(e^x-1)} = \left[\frac{1}{e^x-1} - \frac{1}{e^x} \right]$$

and use the relation,

$$\int_0^\alpha \frac{x^m}{e^x-1} dx = \frac{x^{m+1}}{m+1} \frac{1}{e^x-1} \Big|_0^\alpha + \frac{1}{m+1} J_{m+1}^0(\alpha)$$

Then,

$$\begin{aligned} K_n(\mu, \alpha) &= \frac{e^{-\mu}}{(e^{2\mu}-1)(e^\mu-1)} \int_0^\alpha x^n e^{-x} dx \left[\frac{1}{e^{x+\mu}-1} + \frac{e^\mu}{e^{x-\mu}-1} - \frac{(1+e^\mu)}{e^x-1} \right] \\ &= \frac{e^{-\mu}}{(e^{2\mu}-1)(e^\mu-1)} \left[\int_\mu^{\alpha+\mu} (x-\mu)^n dx \frac{e^{\mu-x}}{e^x-1} + \int_{-\mu}^{\alpha-\mu} (x+\mu)^n dx \frac{e^{-x}}{e^x-1} \right. \\ &\quad \left. - (1+e^\mu) \int_0^\alpha \frac{x^n dx e^{-x}}{e^x-1} \right] \end{aligned}$$

From this, we have

$$\begin{aligned}
 K_n(\mu, \alpha) = & \frac{1}{(e^{2\mu}-1)(e^\mu-1)} \left[\sum_{m=0}^n \frac{1}{m+1} \binom{n}{m} \mu^{n-m} \left\{ e^\mu (-1)^{n-m} \left[\frac{(\alpha+\mu)^{m+1}}{e^{\alpha+\mu}-1} \right. \right. \right. \\
 & \left. \left. - \frac{\mu^{m+1}}{e^\mu-1} \right] + \frac{(\alpha-\mu)^{m+1}}{e^{\alpha-\mu}-1} - (-1)^{m+1} \frac{\mu^{m+1}}{e^{-\mu}-1} \right. \\
 & \left. - (m+1) \left[(-1)^{n-m} e^\mu \zeta_m(\alpha+\mu, \mu) + \zeta_m(\alpha-\mu, \mu) \right] \right. \\
 & \left. + e^\mu (-1)^{n-m} \left[J_{m+1}^0(\alpha+\mu) - J_{m+1}^0(\mu) \right] + \left[J_{m+1}^0(\alpha-\mu) \right. \right. \\
 & \left. \left. + (-1)^{m+1} J_{m+1}^0(\mu) \right] \right\} - \frac{(1+e^\mu)}{n+1} \frac{\alpha^{n+1}}{e^\alpha-1} \\
 & \left. - \frac{(1+e^\mu)}{n+1} J_{n+1}^0(\alpha) - (1+e^\mu) \zeta_n(\alpha, 0) \right] \quad \text{III-(4)}
 \end{aligned}$$

where

$$\begin{aligned}
 \zeta_n(a, b) &= \int_b^a x^n e^{-x} dx \\
 &= -e^{-x} \sum_{r=0}^n x^{n-r} n(n-1) \dots (n-r+1) \Big|_b^a \quad \text{III-(5)}
 \end{aligned}$$

III-C: $J_n(\mu, \alpha)$ and $K_n(\mu, \alpha)$ at low temperature.

We shall evaluate these integrals for two cases,

$$[i] \quad \alpha \gg \mu \gg 1 \quad (\hbar\omega \gg KT)$$

$$[ii] \quad \alpha \gg \mu, \quad \mu \gtrsim 0$$

For the other limiting case of $\mu \gg \alpha$, formula (1) of Appendix II is applicable.

From Equations III-(2) and III-(), we obtain the following simplified expressions;

$$[i] \quad J_n(\alpha, \mu) \approx e^{-2\mu} \mu^{n+1} \sum_{m=0}^n \frac{(-1)^m}{m+1} \binom{n}{m} \quad \text{III-(6)}$$

$$K_n(\mu, \alpha) \approx -2\mu \left[-n! \left(1 + \sum_{s=1}^{\infty} \frac{1}{s^{n+1}} \right) + \sum_{m=0}^n \frac{(-1)^{n+m}}{m+1} (m+1)! \binom{n}{m} \mu^{n-m} \left(\sum_{s=1}^{\infty} \frac{1}{s^{m+1}} - 1 \right) \right] \quad \text{III-(7)}$$

$$: \quad \alpha \gg \mu \gg 1$$

$$[ii] \quad J_n(\alpha, \mu) \approx \frac{2}{e^{2\mu}-1} \left\{ \mu J_n^0(\infty) + \mu^3 \frac{n(n-1)}{3!} J_{n-2}^0(\infty) + \mu^5 \frac{n(n-1)(n-2)(n-3)}{5!} J_{n-4}^0(\infty) + \mu^7 \frac{n(n-1)\dots(n-5)}{7!} J_{n-6}^0(\infty) + \dots \right\} \quad \text{III-(8)}$$

$$\begin{aligned}
 K_n(\alpha, \mu) \approx & \frac{1}{(e^{2\mu}-1)(1-e^{-\mu})} \left[\left[\frac{\mu^{n+1}}{e^\mu-1} \left\{ \sum_{m=0}^n \frac{(-1)^{m+1}}{m+1} \binom{n}{m} [1+(-1)^n] \right\} \right. \right. \\
 & + \sum_{m=0}^n \frac{\mu^{n-m}}{m+1} (m+1)! \binom{n}{m} [e^{-\mu} + (-1)^{n-m}] \left(\sum_{s=1}^{\infty} \frac{1}{s^{m+1}} - 1 \right) \\
 & \left. \left. - n! (1 + e^{-\mu}) \left(1 + \sum_{s=1}^{\infty} \frac{1}{s^{n+1}} \right) \right] \right] \quad \text{III-(9)}
 \end{aligned}$$

$$: \alpha \gg \mu, \quad \mu \gtrsim 0$$

where $J_n^0(\infty)$ is given by formula (3) of Appendix I. Formulae (6), (7), (8) and (9) are sufficient to enable us to calculate $b_{ep}(\mu, \alpha)$ at very low temperatures even in the very far infrared.

Appendix IV

On the Question of Existence of $\cos^2\theta \leq 1$ at the Singularity $\xi=0$

The theoretical calculations of the transition probability rested on the assumption that there exists a $\cos^2\theta$ which satisfies the condition,

$$\delta(\xi) = 1$$

and hence

$$\xi = E(\underline{k}+r\underline{q}) - E(\underline{k}) - rE(\underline{q}) - s\hbar\omega = 0 \quad \text{IV-(1)}$$

$$; r, s = (\pm)$$

and

$$\cos\theta = (\underline{k} \cdot \underline{q} / k q) \quad \text{IV-(2)}$$

The existence of such a $\cos\theta$ was asserted by Wilson (1936) for the processes which do not involve an external electromagnetic field.

We shall show that such a $\cos\theta$ exists also in the presence of the electromagnetic field.

From Equation (1), we have

$$\cos\theta = \left[-sr \frac{m^*\omega}{\hbar kq} + \left(\frac{m^*u_L}{\hbar k} \right) - r \frac{q}{2k} \right] \quad \text{IV-(3)}$$

In comparing the order of magnitude of the three terms on the R.H.S. of Equation (3), we shall use the typical values,

$$m^* \simeq 10^{-27} \text{ (g)}$$

$$u_L \simeq 10^5 \text{ (cm/sec)}$$

$$v_F \simeq 10^8 \text{ (cm/sec)}$$

$$q_0 = \left(\frac{k \Theta}{\hbar u_L} \right) \simeq 10^8 \text{ (cm}^{-1}\text{) for } \Theta \sim 10^2 \text{ }^\circ\text{K}$$

The first term is rewritten as

$$A = \left(\frac{m^* \omega}{\hbar k q} \right) = 2\pi \left(\frac{c}{v_F} \right) \left(\frac{1}{\lambda q} \right) \quad \text{IV-(4)}$$

and the second term as

$$B = \left(\frac{m^* u_L}{\hbar k} \right) = \left(\frac{u_L}{v_F} \right) \simeq 10^{-3} \quad \text{IV-(5)}$$

At ordinary and higher temperatures, the phonons with $q \approx q_0$ are active, and hence we have

$$A \lesssim (2\pi)10^{-2} \quad \text{for } \lambda \gtrsim 1\mu$$

In this case, the third term is the only important one, and any q equal to or smaller than $(2k_F)$ gives us $\cos^2 \theta \leq 1$ satisfying the condition (1). Thus, we have

$$\begin{aligned} \cos^2 \theta &\leq 1 & : & \quad q_0 \geq 2k_F \\ \cos^2 \theta &< \frac{1}{4} \left(\frac{q_0}{k_F} \right)^2 & : & \quad q_0 < 2k_F \end{aligned} \quad \text{IV-(6)}$$

In general, the second of the above two applies when $q_0 \geq 2k_F$, the integral over q must be cut off at $q=2k_F$.

The scattering angle ϕ is defined as

$$\begin{aligned} \cos \phi &= \left(\vec{k} \cdot \vec{k}' / k k' \right) \\ \vec{k}' &= \left(\vec{k} + r\vec{q} + s\vec{p} \right) \\ &\simeq \left(\vec{k} + r\vec{q} \right) \end{aligned} \quad \text{IV-(7)}$$

Then, ϕ is related to θ by the relation

$$\left(k^2 + q^2 + 2r \cos \theta \right)^{\frac{1}{2}} \cos \phi = k \left(1 + r \frac{q}{k} \cos \theta \right) \quad \text{IV-(8)}$$

Then, upon writing

$$q_0 \simeq (2\pi) \left(\frac{3}{4} \pi v_0 \right)^{\frac{1}{3}} \quad \text{IV-(9)}$$

$$k \simeq k_F \simeq (2\pi) \left(\frac{3}{8} \pi v_0 \right)^{\frac{1}{3}}$$

we easily see that the second condition of Equation (6) corresponds to

$$\phi < 78.1$$

in agreement with the usual value of 79° for elastic scattering ($k' = k$), and that the first condition of Equation (6) corresponds to $0 < \phi < \pi$, thus scatterings are possible for all angles.

At low temperatures, the phonons with

$$\hbar u_L q \approx KT \quad \text{IV-(10)}$$

are active, and it is easily seen in Equation (3) that the first term (e.m.-phonon term) can be the most important one. For such a case, we have

$$A \lesssim \frac{1}{T} \quad \text{for } \lambda \gtrsim 1\mu$$

and hence,

$$\cos^2 \theta \lesssim \frac{1}{T^2} ; \lambda \gtrsim 1\mu \quad \text{IV-(11)}$$

so that for $T \gtrsim 1^\circ K$, it is assured that a $\cos^2 \theta \leq 1$ exists.

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